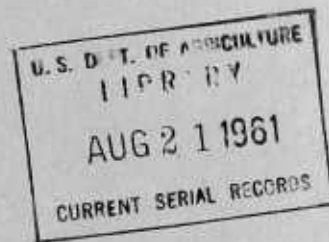


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# SELENIUM IN AGRICULTURE



**Agriculture Handbook No. 200**

**Agricultural Research Service  
U.S. DEPARTMENT OF AGRICULTURE**

**In Cooperation With the  
Geological Survey  
U.S. DEPARTMENT OF THE INTERIOR**

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**SELENIUM**  
**IN**  
**AGRICULTURE**

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By *M. S. Anderson, H. W. Lakin, K. C. Beeson,*  
*Floyd F. Smith, and Edward Thacker*

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56  
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## Foreword

About 1930 the subject of selenium in agriculture came up for consideration by scientists of the United States Department of Agriculture and by various experiment stations of Western States. Numerous bulletins and other publications have been issued on this subject. The publications of the Department on various phases of the selenium problem are, for the most part, out of print or in very short supply. Each of the Department publications presented some segment of the work, but not one dealt with the subject as a whole.

It seems timely that a publication on selenium should be prepared while the services of several people are available who had some part in the initiation and conduct of the research two to three decades ago. In order to develop the contemplated writing project, it was necessary to call upon members of different groups within the Department of Agriculture and to enlist cooperation of the U.S. Department of the Interior.

This Handbook summarizes research that covers especially problems of selenium in soils, its absorption by plants, and the toxic effects of these plants upon animals eating the vegetation.

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# Contents

	Page		Page
History of selenium toxicity.....	2	Occurrence and significance of selenium in plants—	
Organization of governmental research.....	2	Continued	
Geochemistry of selenium in relation to agriculture.....	3	Effect of stage of growth on selenium content....	39
Abundance of selenium in the earth's crust.....	3	Effect of selenium on growth of plants.....	39
Sources of selenium in selenium-rich sedimentary rocks.....	5	Miscellaneous factors affecting the absorption of selenium by plants.....	40
Selenium in native sulfur.....	6	Use and limitations of selenium as an insecticide.....	41
Selenium in sulfides.....	6	Tolerance of insects to selenium.....	42
Transport of selenium in natural waters.....	9	Compatibility with other insecticides.....	42
Behavior of selenium in the zone of weathering.....	11	Kinds of plants treated.....	43
Vertical and lateral distribution of selenium in sedimentary rocks of western United States.....	12	Forms of selenium insecticides.....	43
Selenium anomalies in western United States.....	13	Methods of application.....	43
Sedimentary rocks of Cretaceous age.....	13	Quantity marketed.....	44
Rocks and sediments of various ages.....	23	Dangers of treated plants and soils to animals.....	44
Discussion.....	23	Health hazards from selenium residues.....	45
Chemical determinations of selenium.....	24	Effect of selenium on animals.....	46
Old methods.....	24	Experimental work with laboratory animals.....	50
Current methods.....	24	Experimental work with large animals.....	51
Selenium content of soils.....	27	Protective measures against selenium.....	51
Toxic seleniferous soils—Pedocals.....	27	Favorable effects of selenium in the diet.....	52
Nontoxic seleniferous soils—Pedalfers.....	28	Selenium and human nutrition.....	52
Properties of toxic seleniferous soils.....	30	Conclusions.....	53
Reduction of toxicity by soil amendments.....	33	Management of seleniferous lands.....	53
Occurrence and significance of selenium in plants.....	34	Acquisition of lands.....	53
Species differences in the absorption and accumulation of selenium.....	34	Land management practices.....	55
Selenium indicator plants.....	35	Grazing lease practices.....	55
Selenium converter plants.....	37	The example and the future.....	55
Distribution of selenium in the plant.....	37	Summary.....	55
		Literature cited.....	56
		Appendix.....	63

v

# SELENIUM IN AGRICULTURE

By M. S. ANDERSON, H. W. LAKIN, K. C. BEESON, FLOYD F. SMITH, and EDWARD THACKER

Economic losses from poisonous plants have been reported in the agricultural literature for many centuries. The overall magnitude of such losses will never be known, but to individual herdsmen they often meant financial ruin. Too often, however, losses of this kind have been accepted as one of the hazards of livestock farming.

Traditionally, these livestock losses have been ascribed to toxic compounds or poisonous constituents characteristic of specific plant species. The alkaloids, oxalates, hydrocyanic acid, and nitrates are some of the components of plants long known to be toxic to animals and humans. Generally, the livestock loss was not associated with location as much as with the species of poisonous plants, except inasmuch as there is a location factor associated with the occurrence of specific species.

Beath and associates, in publications of the Wyoming Agricultural Experiment Station (4, 8, 14),<sup>1</sup> describe a number of plants of the State that are a hazard to many livestock owners. Some species of wide distribution that contain toxic organic constituents include death camas, larkspurs, arrowgrass, white loco, lichens, water hemlock, and certain lupines. The reports mentioned above describe each species and tell of its places of growth and when the plant appears. Clinical symptoms of animals poisoned by the different plant species are given and are often followed by descriptions of treatments that should be applied.

It is important to know something about the range plants that are poisonous because of organic chemical groups present, in order properly to distinguish between range poisoning caused by such vegetation and possible poisoning due to inorganic constituents such as selenium compounds as the dominant poisons.

Nutritional problems in animals grazed in specific locations have been recognized; some of these were assumed to be caused by deficiencies of certain essential nutrients in the forage. For example, deficiencies of phosphorus in the soil and forage have long been recognized as a cause of osteomalacia in animals. Prior to 1930, the presence of toxic quantities of a mineral element in

certain plants that grew in soils containing excessive quantities of an element was not accepted as an important factor in animal poisoning. Hence, the discovery that selenium is the toxic factor in "alkali disease" not only supplied the answer to a nutritional problem of long standing but also opened up a whole new concept of soil-plant-animal interrelationships.

For more than a decade, mostly during the 1930's, an intensive investigation was conducted on selenium in rocks, soils, plants, and animal tissues. From the work of the U.S. Department of Agriculture and the activities in certain Western States, particularly by the South Dakota and Wyoming Agricultural Experiment Stations, the agricultural significance of selenium was fairly well established. A large number of Federal and State publications, in addition to articles in scientific journals were published.

This handbook summarizes earlier selenium investigations, and reevaluates the earlier work in the light of later experience.

Many persons took a prominent part in the selenium studies. A few of those in the Department of Agriculture who made important contributions include the following: Horace G. Byers, Henry G. Knight, Thomas D. Rice, W. O. Robinson, H. W. Schoening, W. T. Miller, Anna Hurd-Karrar, A. G. Johnson, John T. Miller, Hazel Munsell, K. T. Williams, R. A. Osborne, and P. L. Gile.

In the State experiment stations the following investigators deserve inclusion in a list of those making notable contributions: Kurt Franke and A. L. Moxon, of South Dakota; and O. A. Beath, of Wyoming.

The names of two scientists outside the United States should also be included. These are George Ancizar Sordo of Colombia, South America (1), and Dr. Figuera of Mexico (208).

Is alkali disease caused by any of the constituents often found to be toxic in plants? In some initial experiments with rats, animals fed fluorine and certain other toxic constituents developed symptoms different from those of alkali disease (23, 133). Knight then suggested that tests be made of the vegetation for selenium. It soon became known that this element was associated in some way with the problem under consideration, for very small quantities were often

<sup>1</sup> Italic numbers in parentheses refer to Literature Cited, p. 56.

present in materials tested. Knight's suggestion, made at an inter-Bureau meeting and followed by the discovery of the elements in the vegetation, touched off a series of investigations that brought selenium into the limelight as a toxic factor to be reckoned with in certain areas of Western States.

It was at once apparent that knowledge of the presence of selenium in soils of a State might be responsible for unwarranted prejudice against agricultural products of that State. Grain and other feeds shipped out of the State might be under suspicion, even though only a small area of land were seleniferous. There might be a decrease also in the selling price of land in areas

where selenium had been found, and county taxes might be adversely affected. As a result the U.S. Department of Agriculture adopted a cautious policy in publishing results and their interpretations, until such time as affected areas could be well delineated and the real hazards of the presence of selenium known.

A Departmental staff was at work promptly after Knight suggested the analysis studies of vegetation and soils for selenium. Time of publication may have little meaning as to priorities of specific discoveries as the research proceeded. Little attempt will be made here to observe such apparent priorities.

## History of Selenium Toxicity

By M. S. ANDERSON

A disease of domestic animals peculiar to certain soils of the Great Plains has been known since early settlement of the Nebraska Territory. Apparently, the first written mention of the disease in this country is found in a statistical report on sickness and mortality in the Army of the United States (116), dated 1857, and published in 1860. Dr. Madison calls attention to a "very fatal disease" among cavalry horses in August 1856 at Fort Randall on the west side of the Missouri River near what is now central South Dakota. He recognized the disease as new, and gave a very satisfactory description of the symptoms. He also correctly ascribed the origin of the trouble to the pasturage. Later the disease was called "alkali disease." This name resulted from the false assumption that saline waters and salt crusts, largely sulfates, were the cause of the trouble. A similar animal disease was known in Mexico more than 200 years earlier. The trouble seemed to be associated with vegetation grown on outwash from certain mines in the vicinity of Irapuato. These mines utilized the Patio process, which involves recovery of silver with mercury. This gave rise to the false assumption that mercury in the local vegetation

was the source of trouble. The disease was known locally as Soliman disease, later shown to be identical with the alkali disease of the United States. Vegetation from a market in Irapuato and from nearby areas showed that plants of the Crucifer family frequently contained enough selenium to constitute a health hazard. Local information indicated that certain people who lived essentially on food produce in the area sometimes had health problems.

Evidence of seleniferous vegetation in other parts of the world far antedates the observations in the Western Hemisphere. There is little doubt that similar troubles were observed by Marco Polo in western China and eastern Turkestan at least as early as 1275 A.D. The following, from a translation by Komroff (98) is of interest:

"It is a fact that when they take that road they cannot venture among the mountains with any beast of burden excepting those accustomed to the country, on account of a poisonous plant growing there, which if eaten by them has the effect of causing the hoofs of the animals to drop off. Those of the country, however, being aware of its dangerous quality, take care to avoid it."

## Organization of Governmental Research

By M. S. ANDERSON

As a result of conferences with many ranchers Kurt W. Franke (58) of the South Dakota Agricultural Experiment Station started work in 1928 on the so-called alkali disease of livestock. Great credit is due him for the approach he made to a study of the problem in South Dakota. His work in that State was later carried on by A. L.

Moxon, who published an excellent paper entitled "Selenium Poisoning" (131). In this report he gave a historical résumé, listing some of the earlier work in which selenium presumably played a part. The earlier work included a report by the Kansas station in 1891 and the Wyoming station in 1893. Peters (144), of the Nebraska

station, mentions related work in 1904; in 1910 the South Dakota station mentions the advisability of conducting cooperative investigations by that State on the so-called alkali disease. These are only a few of the reports in which animal diseases on western ranges are described.

The data, accumulated over a period of years on the poorly understood animal sicknesses on ranges, provided a good background for subsequent studies. The important impact from such records dates from 1931, when the U.S. Department of Agriculture called a conference in Washington, D.C., to discuss the problem, its ramifications, and possible cooperative investigations that might be undertaken.

In 1933 a Presidential order authorized the Secretary of Agriculture to set aside \$35,000 for work on the alkali disease, designated in the Department as the osteoedemic project. Appropriations for this work were later included in the regular budget of the U.S. Department of Agriculture. Such appropriations were continued until the beginning of World War II. Appropriate bureaus and laboratories of the Department took part in the work that involved soils, plants, and animals.

The work on alkali disease was begun during the period of severe economic depression. Under the circumstances the services of several chemists and other scientists were readily obtained. Considerable persuasion was exercised on the former

Bureau of Chemistry and Soils to initiate mass collection of soils to be analyzed in great numbers in a relatively short time. It was not known at that time what place a soil analysis might have in relation to plant composition.

Since various factors influence the availability to plants of other elements in soils, it was assumed that a similar condition exists for selenium. Later, it developed that the selenium contents of certain kinds of plants were of particular importance, whereas other plant species resisted absorption of selenium.

The organization of Federal experimental work established a progressive policy involving collection of samples of soils, vegetation, and other materials; chemical analyses of these materials; and interpretation of the data with respect to a soil-plant-animal relationship. Additional areas were examined each summer, and generalizations regarding the selenium problem were continuously broadened.

When the investigation of alkali disease was begun, no one anticipated that its ramifications might extend far beyond the borders of the United States. However, not only did the trouble extend northward into Canada and southward into Mexico, but soils in other countries and in other entirely different circumstances produce some seleniferous vegetation. Among these are Argentina and Spain (209).

## Geochemistry of Selenium in Relation to Agriculture<sup>2</sup>

By H. W. LAKIN

### ABUNDANCE OF SELENIUM IN THE EARTH'S CRUST

Selenium is one of the dispersed elements, occurring in minute amounts in all materials of the earth's crust and rarely concentrated in any material in amounts above 100 p.p.m. (parts per million). From nine papers published between 1924 and 1952, Fleischer (53) compiled estimates of the abundances of the elements in the earth's crust. The abundance of selenium in igneous rocks was given in three of these papers as 0.09, 0.09, and 0.1 p.p.m.; the estimates for selenium in the earth's crust ranged from 0.03 to 0.8 p.p.m.

Estimates made by geochemists of the average selenium content for the most common rock types are included in table 1. The estimates are probably of the correct order of magnitude—although based on very meager data—because the data available in the literature are much less

numerous for selenium than for those elements readily determined by emission spectrography.

Goldschmidt's value (72, 73) for selenium in igneous rocks—0.09 p.p.m.—is based on considerations of the sulfur-selenium ratio in sulfides of various geologic origin, in which the selenium content is sufficiently high to be measured. He concluded that the average ratio is 6,000 to 1. As his estimate for sulfur in igneous rocks is 520 p.p.m., his average value for selenium is one six-thousandth of this figure, or approximately 0.09 p.p.m. Sindeeva and Kurbanova (166) found 0.1 to 0.37 p.p.m. in 16 of 18 composite samples of various types of igneous rocks from various regions of the Soviet Union. Leutwein and Starke (110) reported from 0.15 to 0.46 p.p.m. of selenium in 5 samples of diabase collected from below the selenium-rich Kupferschiefer in a mine near Wettin about 30 miles northwest of Leipzig in central Germany. Davidson and Powers (42) present 81 analyses of volcanic rocks from Western United States and report that only 1 of 42 samples of

<sup>2</sup> Publication authorized by the Director, U.S. Geological Survey.

TABLE 1.—*Estimates of average selenium content of earth materials*

Material	Authority	Selenium content
		<i>P.p.m.</i>
Igneous rocks-----	Goldschmidt (72)----	0.09
Igneous rocks of U.S.S.R.	Sindeeva and Kurbanova (166).	.14
Limestones-----	Rankama and Sahama (148).	<.1
Limestones and dolomites.	Krauskopf (99)-----	.1-1. (?)
Shales-----	Minami (121)-----	.6
Shales-----	Krauskopf (99)-----	.5-1.0(?)
Shales and clays-----	Vinogradov (198)-----	.6
Sandstones-----	Krauskopf (99)-----	1. (?)
Soils-----	Vinogradov (198)-----	.01
Soils-----	Swaine (176)-----	.1-2.0

crystalline volcanic rocks contained more than 2 p.p.m. selenium; it contained 5 p.p.m.

Beath and others (16) describe a tuff of Eocene age in Wyoming that contained from 12.5 to 187 p.p.m. of selenium. Later work by Everett and Bauerle (51) revealed that the selenium content of the tuff is extremely variable; 198 samples assayed during the course of a drilling program contained less than 50 p.p.m., 6 samples contained between 50 and 120, and 2 contained 120. One surface sample contained 890 p.p.m. Davidson and Powers (42) report analyses of 32 samples of tuffs and vitrophyres from the Western United States; of these, only 3 contained from 0.5 to 3 p.p.m. selenium and the rest contained less than 2 p.p.m.

The selenium content of sea water is extremely low. Byers and others (27) found no selenium in samples of sea water from the Atlantic Ocean off the coast of Ocean City or from the Pacific Ocean at lat. 46°39' and long. 147°47'; but about 0.25 p.p.b. (parts per billion) was found in a sample from Puget Sound off Point No Point. These workers concluded that selenium is not present in sea water in amounts in excess of 0.25 p.p.b., the lower limit of their analytical method, except near the mouths of streams carrying selenium. Although Goldschmidt and Strock (74) found 4 p.p.b. of selenium in a sample of sea water from the North Sea, Byers and others attributed this selenium to the Elbe River, which carries minute amounts of selenium. Lakin and Byers (101) found 3 p.p.b. of selenium in 4 samples of water from the Gulf of California 30 and 70 miles south-east of the mouth of the Colorado River. The selenium content of Japanese coastal waters ranges from 4 to 6 p.p.m. (Ishibashi and others, 92). The relative absence of selenium in sea water and its presence in most sea-floor samples examined are presumably the result of the precipitation of selenium as a basic ferric selenite.

The selenium content of limestones is variable, but usually low. Goldschmidt and Strock (74) reported less than 0.1 p.p.m. in a composite of 32 Devonian limestones from Germany. Byers (23) found from 0.3 to 6 p.p.m. in 3 samples of Fort Hays limestone in Kansas; Moxon and others (130) found a maximum of 3 p.p.m. in 5 composite samples of the same formation in South Dakota. The Smoky Hill member of the Niobrara formation, described as a calcareous marl, in many places contains as much as 20 p.p.m. selenium. Moxon and others (128) found 0.25 and 0.8 p.p.m. selenium in limestones of Mississippian and Ordovician age. Knight and Beath (97), on examination of limestones in Wyoming, found 14.3 p.p.m. in limestone beds of the Phosphoria formation, 6.68 in a limestone member of the Frontier formation, and 1.54 of selenium in a limestone member of the Thaynes formation. Fleming and Walsh (55) reported a limestone containing 2 p.p.m. of selenium in Ireland.

Shales commonly contain more selenium than other sedimentary rocks. For example, Minami (121) reported a composite of 36 European Paleozoic shales as containing 1.2 p.p.m. selenium, a composite of 14 Japanese Paleozoic shales as containing 0.24 p.p.m., and a composite of 10 Japanese Mesozoic shales as containing 0.38 p.p.m. Byers (23), whose method of analysis permitted the detection of 0.1 p.p.m. of selenium, reported that selenium was detected in all 500 samples of Pierre shale. Ancizar-Sordo (1) reported a seleniferous area in Sutamarchan, State of Boyaca, Colombia, in which the soils were developed from a gray shale. The 2 samples of shale examined contained 1 and 14 p.p.m. selenium, respectively. Fleming and Walsh (55) assumed the source of selenium in Irish lacustrine soils containing 30 to 1,200 p.p.m. selenium to be a pyritic shale of early Carboniferous age containing as much as 28.5 p.p.m. The Kupferschiefer in central Germany is a copper-rich black shale of Permian age that has been reported by Leutwein and Starke (110) to contain as much as 15 p.p.m. selenium. Sindeeva and Kurbanova (166) give 0.3, 0.74, and 9.0 p.p.m. for the selenium content of 3 samples of shale of Silurian age from the Baltic region. Beath and others (16) report as much as 680 p.p.m. in a sample of vanadiferous shale zone of the Phosphoria formation in western Wyoming; Davidson and Gulbrandsen (41) report samples of mudstone from the Phosphoria formation containing more than 1,500 p.p.m. selenium.

Sandstones are usually more permeable than limestones and shales, and their gross composition is more variable. These properties are reflected in the selenium content of sandstones. Moxon (123) failed to find any selenium in 10 samples of sandstones in South Dakota, ranging from Cretaceous to Tertiary in age. Knight and Beath



(97) examined sandstones containing carbonaceous shale bands in the Medicine Bow formation in Wyoming and found that the carbonaceous shale band contained 14.39; sandstone adjacent to the shale, 112.8; and the sandstone 10 inches from the shale-sandstone contact, only 2.86 p.p.m. of selenium. Beath and others (16) describe a sandstone, presumably of Tertiary age, from Carbon County, Wyo., that contains 112 p.p.m. of selenium, 91.4 p.p.m. being water soluble. One may conclude that the selenium content of sandstones is locally variable; local enrichment may occur because of precipitation of selenium from ground waters moving through the beds long after their deposition. Krauskopf (99) discussed briefly the processes of enrichment of selenium and other metals in red beds. The same processes probably are operative in sandstones containing selenium associated with uranium on the Colorado Plateau (Coleman and Delevaux, 37).

The selenium content of phosphate rocks is variable, ranging from less than 0.1 to 55 p.p.m. in 96 representative samples reported by Rader and Hill (147). Davidson and Gulbrandsen (41) report up to 300 p.p.m. selenium in phosphate rock from the Phosphoria formation. There is no consistent correlation between selenium and the pyrite or organic matter content of these rocks; although the dark-colored pyritiferous phosphate rock of the Phosphoria formation in Idaho is highest in selenium content, the dark-colored pyrite-free rock is medium, and the light-colored rock is lowest, the range given by Rader and Hill (147) is from less than 0.9 to 30 p.p.m. of selenium. These authors reported that 0.6 percent of the total selenium was water-soluble in one sample of an Idaho phosphate rock. They also found that primary phosphate deposits are generally higher in selenium (average of 41 samples, selenium less than 10.9 p.p.m.) than secondary deposits (average of 34 samples, selenium less than 2 p.p.m.), and suggest it has been leached from the secondary deposits. According to these authors only a small portion of the selenium in the raw materials from which superphosphate and phosphoric acid are made is found in the finished products.

## SOURCES OF SELENIUM IN SELENIUM-RICH SEDIMENTARY ROCKS

Various processes have been suggested for the anomalous concentrations of selenium in sedimentary rocks. Some suggested processes of concentration are (1) precipitation of selenium from volcanic emanations by rain; (2) deposition of erosional products from volcanic sulfur, seleniferous tuffs, and sulfide deposits; and (3) precipitation of selenium from streams or ground water

carrying unusual quantities of selenium from older seleniferous sediments.

Selenium is one of the volatiles in magmas, and much of it escapes into the air during volcanic activity. Although much of the selenium in the earth's crust is contained in disseminated pyrite and in sulfide ores, the anomalous seleniferous content of the sedimentary rocks of Western United States may be accounted for by introduction of the selenium into the sediments from the volatile products during a long period of volcanism. During the period from Devonian time, 260 million years ago, through Miocene time, approximately 10 million years ago (46), that part of this continent west of the present Mississippi River was at many times below sea level, closed on the northeast by the Canadian shield, and closed on the east by the Appalachian uplift. An uplift at the approximate location of the present western coast or perhaps farther west was in a state of intermittent volcanic activity (46). The normal eastward sweep of the winds must have carried the ash and gases from this volcanism across the region occupied by our continent. The selenium in these gases was probably oxidized to selenium dioxide, carried down by rain and eventually precipitated as a basic ferric selenite or reduced to  $\text{Se}^{\pm}$  and precipitated with pyrite. The semi-closed nature of the sea prevented oceanic currents from conveying fine sediments away. As a consequence, one may assume that selenium accumulated in these sediments that would eventually become sedimentary rocks. Activity of selenium-oxidizing and -reducing bacteria (Zo Bell, 212, p. 166) on the floor of such inland seas could locally render selenium soluble by oxidative action or insoluble by reductive action, and thus cause further localization of the selenium in the sediments.

Vinogradov (197) compares the soils of the Russian plains with those of North America, but states: "However, on the Russian plains, we do not find those local concentrations of products of volcanic origin such as boron, arsenic, selenium, and some other chemical elements. What happens in soils in the United States of America could be attributed to the different histories of these two platforms." Goldschmidt (73) presents a slightly different picture as follows: "It appears that the great igneous activity that has occurred in the Cordilleran region of North America has been instrumental in producing numerous vein deposits of selenides, and also, perhaps through volcanic emanations, adding considerably to the small amounts of selenium normally present in sediments." If the abnormal amounts of selenium found in our soils today have their principal origin in volcanic emanations or in an abundance of sulfide deposits rich in selenium that is subsequently distributed during weathering, magmatic activity in one form or another is assumed by many geologists to be the primary source of the selenium of our western Plains.

## SELENIUM IN NATIVE SULFUR

In an oxygen-deficient environment, selenium is associated with sulfur; it is found in or associated with sulfides and volcanic sulfur. The selenium contents of some samples of volcanic sulfur are listed in table 2. The 2 samples from Kilauea containing 1,400 and 2,200 p.p.m. selenium, reported by Byers and others (28), represent recent deep-seated activity. The 4 samples of sulfur collected by T. S. Lovering (table 2 footnote) in 1957 give some insight into the variation of the selenium content of the Hawaiian sulfurs: The sulfur from the "Blowhole" cinder cone (Se 1,600 p.p.m.) and the New Pit crater (Se 1,600 p.p.m.) are thought to represent magmatic sulfur from depth; the sulfur from the Spatter cone (Se 900 p.p.m.) may be reworked near-surface sulfur, as the eruption was feeble and of short duration; the sulfur from the sulfur bank (Se 4 p.p.m.) at Kilauea has probably been moved many times. This suggests a partial separation of selenium from sulfur during sublimation. The low selenium content of the sulfurs from Mexico, West Indies, and Iceland may represent residual selenium-poor fractions or may be indicative of selenium-poor provinces.

Some old analyses of selenosulfur reported from the literature by Palache and others (1, p. 142; 141) show: Kilauea, Hawaii, 5.18 percent; New Zealand, 0.30 and 0.19 percent; Lipari Islands, 0.28 and 0.27 percent; and Vulcano, Lipari Islands, 1.03 and 0.83 percent selenium. Some new determinations of five samples of selenosulfur from Vulcano range from 0.07 to 0.18 percent selenium, with an average of 0.13 percent (Garavelli, 67).

The selenium in Hawaiian soils is probably derived from volcanic emanations (Byers and others, 28). Postulation of this source is supported by the demonstrated presence of selenium in the gases given off by Kilauea (0.005 mg. in 600 ml. of gas) and its relative absence in Hawaiian lava (less than 0.1 p.p.m.).

Data on selenium in sulfur from sedimentary rocks are strangely lacking. Although Byers and others (27, p. 66) state that the absence of selenium in secondary sulfur has been repeatedly demonstrated, they neither give any data nor state the source of the sulfur examined. Strock (175) reports the presence of selenium in sulfur of volcanic origin and then states: "On the other hand, the large occurrences of sulphur in sedimentary rocks are either free from selenium (Louisiana) or contain only traces of the element (Sicily)." These observed differences in the selenium content of sulfur of volcanic origin and sulfur of sedimentary origin fit the chemical behavior of the two elements: in the weathering zone sulfur is readily oxidized to sulfate and is mobile; only under special circumstances is selenium oxidized to the soluble mobile selenate.

## SELENIUM IN SULFIDES

Because of the similar ionic radii of sulfide ion ( $S^{2-}$ ) and selenide ion ( $Se^{2-}$ ), selenium readily replaces sulfur in sulfide minerals. Although some selenium is found in naturally occurring selenides of silver, copper, lead, mercury, and nickel in many parts of the world (Earley, 47), the bulk of the selenium in the earth's crust occurs in sulfide minerals. The annotated bibliography on the

TABLE 2.—*Selenium in sulfur*

Location	Description	Reference	Selenium
Colorado	Crude sulfur, Vulcan Mine, Gunnison County	(23)	P.p.m. 8,350
Kilauea, Hawaii	Lava of 1919 acted upon by solfatara gases, 1920	(28)	1,400
	Sulfur from the Southwest Crack at the great Solfatara collected in 1921 before the great overflow of March 7, 1921.	(28)	2,200
	Sulfur from "Blowhole" cinder cone, 1955 lava	(1)	1,600
Hawaii	Sulfur from New Pit crater 1955, Kalapana Rd.	(1)	1,600
	Sulfur from Spatter cone on road cut NE of Kalapana—1955 eruption.	(1)	900
	Sulfur bank, Kilauea volcano	(1)	4
Mexico	Sulfur from Popocatepetl collected on the border of the States of Mexico and Puebla.	(208)	.6
	Sulfur from Popocatepetl Industrial Museum, Mexico City	(208)	.5
	Sulfur from Citlaltepēt, State of Puebla	(208)	10
West Indies	Sulfur from El Chickosa, State of Chiapas	(208)	0
	Sulfur from Montserrat	(27)	5
Alaska	Sulfur and arsenic sulfide incrustation, Fumarole No. 135, Valley of 10,000 Smokes.	(211)	1,200
Iceland	Sulfur from hot springs deposits at Krisuvik	(63)	18.9

<sup>1</sup> Sulfur collected by T. S. Lovering in January 1957, and analyzed by W. A. Bowles, Jr.; the sulfur from the "Blowhole" cinder cone and New Pit crater is thought to be from a deeper source than that from the Spatter cone.

geology of selenium by Luttrell (114) offers a coverage of the literature on selenium minerals.

The distribution of selenium in various sulfides throughout the world, shown in table 3, is taken from the comprehensive compilation by Michael Fleischer (54). Data recently published by Takimoto and others (180) on Japanese sulfides do not alter the general distribution for the sulfides listed in table 3. Some galenas are high in selenium, however, and Davidson (40) has reported more than 1 percent selenium in some stibnite ( $\text{Sb}_2\text{S}_3$ ) samples and more than 0.1 percent in many others. Edwards and Carlos (48) found 7 to 9 p.p.m. selenium in four samples of stibnite from Australia. These values are higher than the majority of their values for sphalerite and galena. Davidson (40) suggests that the selenium content of stibnite may normally be relatively high.

The data in table 3 show a concentration of selenium in all the types of sulfide minerals examined; only 4 of 233 samples show no selenium in measurable amounts. Selenium is markedly higher in the sulfide minerals from sedimentary rocks of Western United States (table 4), as reported by Coleman and Delevaux (37). To illustrate, the highest value for selenium in pyrite in table 3 is 300 p.p.m.; in contrast, the pyrite from the sandstone-type uranium deposits in the Colorado Plateau carries as much as 3 percent. Correspondingly, only 13 (12 percent) of the 115 samples of pyrite in table 3 contained more than 100 p.p.m. Se, whereas 29 of the 92 samples (31 percent) from the Colorado Plateau contained more than 100 p.p.m. This may be a further indication that the western part of the United States is anomalously high in selenium.

Selenium is localized in some sulfide deposits. Coleman and Delevaux (37) describe a "persistent 'galena' band developed in the vanadium deposits within the Entrada sandstone [Rifle District, Garfield County, Colo.] composed of galena-clausthalite ( $\text{PbS}$  and  $\text{PbSe}$ ) in solid solution \* \* \* the average selenium content of nine samples is 12.2 percent with a high of 18 percent." Bergenfelt (18) found 1.5 percent selenium in galena from northern Sweden. Although other examples can be cited, the role of selenium-rich sulfides in the formation of seleniferous soils is difficult to evaluate.

In the milling of sulfide-ore deposits, slime dumps rich in sulfides accumulate. These sulfide-rich slime dumps are commonly near stream beds, and the slimes may be carried by floods to be deposited on alluvial plains below the mill. Three examples are known of the deposition on flood plains of selenium-bearing slimes from mining operations.

One sample, described by Byers (25), is located in the valley of the Guanajuato River, State of Guanajuato, Mexico, where chronic poisoning of domestic animals has resulted. During the 200

years that a silver mine near the river has been in operation, the slime dumps have been periodically eroded away by the Guanajuato River and deposited on the flood plain downstream from the mine. Byers reported that a sample of water collected 0.25 mile below the slime dump contained 0.2 p.p.m. soluble selenium and that this water was used for irrigation. The surface soils of the alluvial plain contained 1 to 6 p.p.m. selenium; adjacent soils not subject to flooding and samples below 12-inch depth in the flood plain contained 0.1 to 0.4 p.p.m. selenium. This report is of interest because the selenium content of the sulfides is not high. Three samples of the ore—wastes high in marcasite and other sulfides and of the slime—contained, respectively, 16, 7, and 4.6 p.p.m. of selenium.

Another area of flood plain contamination by selenium-rich sulfide slimes has been observed near Park City, Utah (Lakin and Byers, 102). Ore from nearby mines is milled in Park City; the silver-, gold-, lead-, and zinc-rich concentrates are shipped to Salt Lake City, and the rejected slimes are collected in settling basins along Silver Creek. Samples of the ores contained as much as 540 p.p.m. of selenium, and samples of the slimes ranged in selenium content from 25 to 125 p.p.m. The selenium content of silt samples from the stream bed ranged from 70 p.p.m. for those below the settling basin on Silver Creek to 20 p.p.m. in silt, 14 miles below the basins at the confluence of Silver Creek with the Weber River. Although the Weber carries 3 to 5 times as much water as Silver Creek, a sample of sediment along the Weber 1 mile below the mouth of Silver Creek contained 5 p.p.m. of selenium. A sample of water from Silver Creek contained only 0.001 p.p.m. of selenium, and the vegetation collected in the flood plain was of relatively low selenium content (0.5 to 70 p.p.m.). These mines had been open about 70 years when the streams were sampled. Perhaps, pollution by wastes from these mines will also cause an agricultural problem in the years ahead.

The third example of flood plain contamination with seleniferous material is cited by Trelease and Beath (185) from unpublished work of Beath. The Jordan River in Owyhee County, Idaho, drains a mining district that has produced large quantities of silver and gold ore. The authors state: "One of the most abundant of the silver ores in the district was naumannite ( $\text{Ag}_2\text{Se}$ ) containing 23 percent selenium." Selenium poisoning has occurred on the grasslands of the flood plains below the mines. The silt deposited on these plains contained from traces to 25 p.p.m. Se, and grass growing in it contained up to 116 p.p.m.

These examples of the erosion of selenium-bearing waste from mining operations show the rapid concentrations of selenium in the sediments below mine workings and grossly exaggerate the selective solution and precipitation that might occur in the normal weathering of sulfide

TABLE 3.—*Selenium in some sulfide minerals*<sup>1</sup>

Minerals	Maximum concentration	Samples in each selenium concentration of—									Total samples
		5,000 p.p.m. or more	1,000–4,999 p.p.m.	500–999 p.p.m.	200–499 p.p.m.	100–199 p.p.m.	50–99 p.p.m.	10–49 p.p.m.	<10 p.p.m.	Not found	
	<i>P.p.m.</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>
Sphalerite.....	900			1	3		1	9	27		41
Chalcopyrite.....	2, 100		2	2	7	5	4	22	1		43
Pyrite.....	300				3	10	16	43	40	3	115
Marcasite.....	11							1	7	1	9
Pyrrhotite.....	63						3	11	6		20
Troilite.....	132					1	1				2
Arsenopyrite.....	57						1	2			3

<sup>1</sup> Data from Fleischer (54).TABLE 4.—*Selenium in sulfide minerals from some rocks of the Western United States*<sup>1</sup>

Minerals and source	Maximum concentration	Samples in each selenium concentration range of—										Total samples
		1 percent or more	5,000–9,999 p.p.m.	1,000–4,999 p.p.m.	500–999 p.p.m.	200–499 p.p.m.	100–199 p.p.m.	50–99 p.p.m.	10–49 p.p.m.	3–9 p.p.m.	<3 p.p.m.	
	<i>Percent</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>	<i>Number</i>
Sedimentary rocks:												
Pyrite.....	3	2	3	7	2	5	9	9	19	21	33	110
Pyrite marcasite.....	5	2	4	9	2	4	4	7	8	8	12	60
Marcasite.....	. 65		1			1	1		1	2		6
Hydrothermal vein deposits and intrusive rocks:												
Pyrite.....							2	3	3	1		9

<sup>1</sup> Data from Coleman and Delevaux (37).

bodies, but represent only acceleration of the same processes.

Native selenium has resulted from the oxidation of selenides and seleniferous sulfides in the Colorado Plateau. Thompson and others (182) report two occurrences of native selenium associated with uranium and vanadium ores of the sandstone-type on the Colorado Plateau. Davidson (40) reported elemental selenium associated with uranium ores of the Powder River Basin, Wyoming, and Thompson and others (182) have reported elemental selenium in the Black Hills. Trites and Lakin (191), in a study of the zone of oxidation in seleniferous pyritic sandstone-type uranium deposits in the Gas Hills area in the central part of Wyoming and the Baggs area on the Wyoming-Colorado border, found the rock highest in selenium content was sandstone containing red elemental selenium with varying amounts of hydrous iron oxide that may contain some basic ferric selenite. These pink sandstones contained as much as 2.7 percent selenium. Coleman and Delevaux (37) have reported the presence of soluble selenium in mine and ground waters.

## TRANSPORT OF SELENIUM IN NATURAL WATERS

In the western United States both solution and redeposition of selenium are now taking place. The meager data available on the Colorado River Basin are sufficient to illustrate these phenomena. An outline of the Colorado River Basin with the location of sampling points is given in figure 1. The selenium contents of samples of the Colorado River and some of its tributaries are given in table 5. The upper reaches of the Colorado and its tributaries are usually selenium-free. The selenium content rises in irrigated areas and may be derived from the leaching of irrigated seleniferous lands. The high selenium content of water from drainage ditches of irrigated areas along the Gunnison and Colorado Rivers (table 6) as compared to the relatively low selenium content of these rivers shows that the water draining irrigated mildly seleniferous lands is much enriched in selenium. Salt crusts on walls of drainage ditches in the same areas contain 16 to 260 p.p.m. (See table 7.)

Much selenium is moved annually by these streams. From 2.4 to 5.9 tons of selenium per month passed a water gage station on the Gunnison River just above its confluence with the Colorado River during a 6-month period, April 1 to September 30, 1936 (table 8). The total for the 6 months was 23.5 tons. The variation with time suggests an increasing return of seleniferous irrigation-drainage waters to the river in July, August, and September. The high spring value probably represents a flushing-out of salts deposited in the fall on the walls and floor of drainage ditches.



Figure 1.—The Colorado River Basin showing location of sampling points in tables 5 and 6.

The selenium content of a sample of Colorado River water collected at Yuma, Ariz., was 4 p.p.b. (parts per billion) (table 5). Lakin and Byers (101) reported 3 p.p.b. Se in waters from the Gulf of California 30 and 70 miles southeast of the mouth of the Colorado River. The selenium content of composite sea-floor samples ranged from none detected to 0.4 p.p.m.; the highest value was in a composite core 120 miles southeast of the mouth of the Colorado River.

From these data it is evident that selenium is being carried seaward by the Colorado River and is eventually deposited in the muds of the sea floor. It is also evident that irrigation practices hasten the movement of selenium. The use of these seleniferous waters downstream by other irrigation projects may create additional seleniferous agricultural areas, but the data available in the literature are inadequate to evaluate the hazards involved.

Few data are available on the Missouri-Mississippi River basin. Byers (23) reported as much as 1,200 p.p.b. in drainage water from the Belle Fourche irrigation project in Butte County, S. Dak. Sea-floor samples from the Gulf of Mexico range in selenium content from 0.6 to 1.0 p.p.m. (Lakin and Byers, 101). Apparently selenium is moving downstream in this river sys-

TABLE 5.—*Selenium content of water from the Colorado River and some of its tributaries*

Laboratory No.	Stream and location	Reference	Se
			<i>P.p.b.</i>
B-14417	Colorado River, near Cameo, Colo.	Williams and Byers (206, table 1)	0
B-14423	Gunnison River, near Cimarron, Colo.	do	0
B-15197	Uncompahgre River, 5 miles south of Ouray, Colo.	do	0
B-15196	Uncompahgre River, 13 miles south of Montrose, Colo.	do	0
B-14422	Uncompahgre River at Colona, Colo. (Dec. 1934)	do	3
B-15201	Uncompahgre River at Colona, Colo. (May 1935)	do	2
B-14427	Gunnison River, ½ mile north of Delta, Colo.	do	7
B-14420	Gunnison River, near Redlands (near Grand Junction), Colo.	do	80
B-14420A	Colorado River, near Grand Junction, Colo.	do	30
B-18090	Paria River, Lees Ferry, Ariz.	Byers and others (27, table 13)	1
B-18089	Little Colorado River, Grand Falls, Ariz.	do	1
	Colorado River, Topock, Ariz.	Williams and Byers (206, table 1)	0
B-18003	Williams River, Planet, Ariz.	Byers and others (27, table 13)	0
B-20536	Gila River, Coolidge Dam, Ariz.	do	1
B-20537	Gila River, Gillespie Dam, Ariz.	do	2
B-20535	Colorado River, Yuma, Ariz.	do	4

TABLE 6.—*Selenium content of water from drainage ditches of irrigated areas along the Gunnison and Colorado Rivers*<sup>1</sup>

Laboratory No.	Field No.	Location	Se
			<i>P.p.b.</i>
B-14421	6	Drainage ditch in Montrose, Montrose County, Colo.	700
B-14424	9	Main lateral, 1 mile south of Chipeta, Montrose County, Colo.	1,050
B-14426	11	Relief drainage ditch, 2 miles east of Montrose, Montrose County, Colo.	320
B-14419	3	Main drain, 1.5 miles east of Loma, Mesa County, Colo.	630
B-15203	9	Surface drainage, 1 mile north of Mack, Mesa County, Colo.	7
B-15204	11	Surface drainage near Loma, Mesa County, Colo.	3
B-14418	2	New drain, 4 miles north of Mack, Mesa County, Colo. (1934)	1,980
B-15202	8	New drain, 4 miles north of Mack, Mesa County, Colo. (1935)	2,680

<sup>1</sup> Data from 206, table 1.TABLE 7.—*Selenium content of salt crusts on drainage ditches of irrigated areas along the Gunnison and Colorado Rivers*<sup>1</sup>

Laboratory No.	Field No.	Location	Se
			<i>P.p.m.</i>
B-14412	18	Near main lateral, 1 mile south of Chipeta, Montrose County, Colo.	100
B-14442	28	Main drain, 1.5 miles east of Loma, Mesa County, Colo.	16
B-14439	25	6.5 miles east of Fruita, Mesa County, Colo.	260
B-15085	4	Sec. 15, T. 9S., R. 103W., Mesa County, Colo.	52

<sup>1</sup> Data from 206, table 2.

TABLE 8.—*Selenium in water from 3 stations on the Colorado and Gunnison Rivers*

Laboratory No.	Stream	Location	Composite water sample for dates shown	Runoff in acre-feet of water <sup>1</sup>	Se <sup>2</sup>	Se per month (calculated)
					<i>P.p.b.</i>	<i>Tons</i>
B-20269	Colorado River	Cameo, Colo	Apr. 11-30, 1936	329, 400	0	-----
B-20270	do	do	May 1-31, 1936	1, 168, 000	0	-----
B-20271	do	do	June 1-30, 1936	942, 500	0	-----
B-20272	do	do	July 1-31, 1936	347, 500	0	-----
B-20469	do	do	Aug. 1-31, 1936	234, 800	1	0. 32
B-20470	do	do	Sept. 1-30, 1936	122, 200	1	. 17
B-20273	do	Grand Junction, Colo.	Apr. 11-30, 1936	( <sup>3</sup> )	5	-----
B-20274	do	do	May 1-31, 1936	( <sup>3</sup> )	2	-----
B-20275	do	do	June 1-30, 1936	( <sup>3</sup> )	0	-----
B-20276	do	do	July 1-31, 1936	( <sup>3</sup> )	1	-----
B-20467	do	do	Aug. 1-31, 1936	( <sup>3</sup> )	5	-----
B-20468	do	do	Sept. 1-30, 1936	( <sup>3</sup> )	10	-----
B-19565	Gunnison River	do	Apr. 1-30, 1936	291, 500	15	5. 9
B-19566	do	do	May 1-31, 1936	629, 300	5	4. 4
B-19567	do	do	June 1-30, 1936	301, 900	10	4. 1
B-20277	do	do	July 1-31, 1936	72, 680	25	2. 4
B-20465	do	do	Aug. 1-31, 1936	79, 370	25	2. 7
B-20466	do	do	Sept. 1-30, 1936	53, 470	55	4. 0

<sup>1</sup> Calculated from data given in 195, p. 222.

<sup>2</sup> Data from 27, table 13.

<sup>3</sup> No record.

tem from the large areas of seleniferous lands drained by the Missouri River and its tributaries.

Movement of selenium in other areas is given by De Salas (43), who has examined a number of ground and surface waters in Argentina and found selenium ranging from 1 to 67 p.p.b. Surface waters were generally free of selenium; the highest value reported was 19 p.p.b. In the provinces of Cordoba and Catamarca, ground waters contained, respectively, 16 to 39 p.p.b. for the 3 samples examined, and 7 to 67 p.p.b. for 5 samples.

# BEHAVIOR OF SELENIUM IN THE ZONE OF WEATHERING

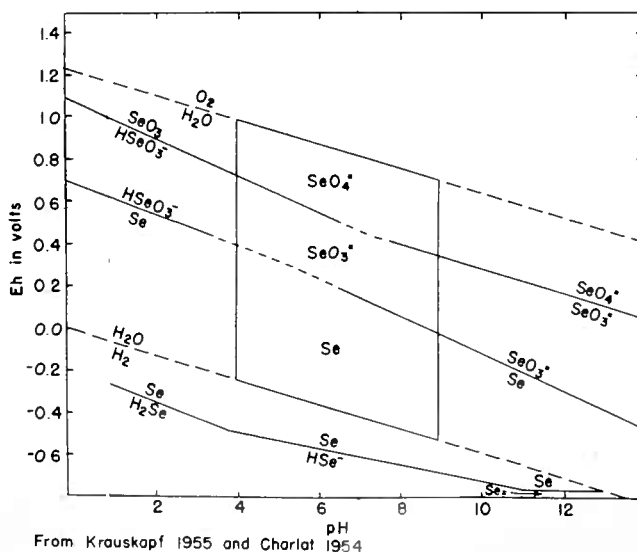
The presence of water-soluble compounds of selenium in Western United States is demonstrated by its presence in water of rivers, wells, and springs. In Hawaii and Puerto Rico, however, selenium, although present, seems to be fixed in certain soils and unavailable to plants.

The behavior of selenium in various environments may best be determined by an examination of the oxidation potentials for its various oxidation states as a function of pH. Krauskopf (99) calculated the oxidation potentials at varying pH for selenium ions at a concentration of  $10^{-7}$  mole per liter. These data are given in figure 2. Krauskopf (99) states:

"Each line on the diagram represents equilibrium between the oxidized form written above the line and the reduced form written below it \* \* \*. The space between two lines \* \* \* is the stability field of the ion or molecule shown on the upper side

of the lower line and the lower side of the upper line. The area enclosed by heavy lines shows the normal range of surface conditions." The lower line for  $\text{Se}^0\text{--Se}^-$  is taken from Charlot (34) and is for molar solutions. The sign of the redox potential is given according to the European convention and is opposite to that of Latimer (107).

These data show that  $\text{H}_2\text{Se}$  is unstable in the presence of moist air. When it is liberated from  $\text{FeSe}$  by hydrochloric acid, it decomposes to elemental selenium and water (Trites and Lakin, 1971). The presence of selenium as a pink halo



**Figure 2.**—Variation of oxidation potentials of the oxidation states of selenium as a function of pH.



around oxidizing sulfide bodies is due to this instability. The presence of elemental selenium in volcanic sulfur is another example of ready oxidation of the sulfide.

Selenium is also oxidized from  $\text{Se}^0$  to  $\text{Se}^{+4}$  ( $\text{SeO}_3^{2-}$ ) with relative ease. Selenites may be readily formed in alkaline to mildly acid conditions; thus, selenites should be found in nature. Williams and Byers (207) demonstrated that when extremely dilute solutions of selenites react with ferric chloride, a very insoluble precipitate is formed that approximates the composition of basic ferric selenite ( $\text{Fe}_2(\text{OH})_4\text{SeO}_3$ ); the ratio of iron to selenium, however, is not constant. Byers and coworkers give numerous examples of the association of selenium with ferruginous precipitates. The presence of 12 p.p.m. of selenium in Hawaiian soils under an annual rainfall of about 100 inches is considered by Byers and others (27) as an example of the occurrence of this iron-selenium complex.

In strongly acid conditions—one molar with respect to  $\text{H}^+$ —the oxidation potential for  $\text{SeO}_3^{2-}$  to  $\text{SeO}_4^{2-}$  is + 1.15 volts. In acid solution, therefore, very strong oxidants are required to oxidize selenium to selenic acid; concentrated nitric acid does not oxidize it quantitatively. But at pH values of about 7 and greater, the difference between the  $\text{SeO}_3^{2-}$ — $\text{SeO}_4^{2-}$  couple and  $\text{H}_2\text{O}$ — $\text{O}_2$  couple is almost 0.4 volts, a difference large enough to permit the oxidation of  $\text{SeO}_3^{2-}$  to  $\text{SeO}_4^{2-}$

by oxygenated water. If the selenite selenium were distributed in porous alkaline moist materials, its oxidation by air might proceed at a measurable rate.

Although Goldschmidt and Strock (74) reported the presence of selenates in Chilean nitrates and Williams and Byers demonstrated their presence in South Dakota soils in 1936, it is still tacitly assumed in some current literature that selenates are very unstable in nature and that selenium rarely occurs in this form. The ready reduction of selenates by halogen acids is more frequently mentioned than is the fact that dilute selenic acid solutions do not react appreciably with such relatively strong reducing agents as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , and  $\text{Fe}^{+2}$  in the absence of halogen acids (Latimer, 107). Recently Sindeeva (165) stated that the selenates are very easily reduced to selenites and to free selenium in nature. The fact is, however, that in an alkaline oxidizing environment selenates are stable.

From these considerations one might make the following predictions: (1) In regions of alkaline soils—and particularly in regions of low rainfall—the selenium would occur, in part at least, as selenate; this selenate selenium would be soluble, available to vegetation, and readily transported in ground waters; (2) in regions of acid environment, selenium, if present, would be found in ferric hydroxide precipitates—quite stationary, and presumably of low availability to plants.

## Vertical and Lateral Distribution of Selenium in Sedimentary Rocks of Western United States<sup>3</sup>

By H. W. LAKIN

In an investigation of the so-called “alkali disease” of livestock, a preliminary field survey was made in the summer of 1931 by Kurt W. Franke, chemist, T. D. Rice, soil scientist, A. G. Johnson, plant pathologist, and H. W. Schoening, veterinarian (59), to evaluate the economic importance of the disease, its geographical distribution, and possible soil and plant relationships. Every case of the disease investigated by them in the central and southwestern parts of South Dakota, parts of northern Nebraska, and the eastern part of Wyoming occurred on soils called Pierre clay or Pierre clay loam that were developed from the Pierre shale. This significant observation directed the attention of all workers interested in the alkali disease problem to the importance of the parent material from which seleniferous soils are developed. It was soon

found that in addition to the Pierre shale, numerous other geologic formations are sufficiently seleniferous to form soils that are potential hazards to farm and ranch animals.

The Pierre shale is of Cretaceous age and has an enormous extent, cropping out in North Dakota, South Dakota, Nebraska, Montana, Wyoming, Colorado, and New Mexico; rocks of equivalent age and similar lithology are known in Utah. Byers (23) reported on about 500 samples representing strata in the recognized subdivisions of Pierre shale that crop out in Nebraska and South Dakota. Selenium was found in every sample; Byers published only a small part of the analytical data but stated that the quantities of selenium found ranged upward through 100 p.p.m. This early concept of the relation of the selenium content of the soils to that of the geologic formation from which the soils are derived has been developed and expanded by workers who followed Byers. The work in South Dakota of A. L.

<sup>3</sup> Publication authorized by the Director, U.S. Geological Survey.



Moxon and his associates at the South Dakota Agricultural Experiment Station is the most complete study of these relationships, and the data from their investigations form the chief bases of the generalizations made in this review.

## SELENIUM ANOMALIES IN WESTERN UNITED STATES

Data in geologic literature show that the selenium content of various rock types, sediments, and soils is locally variable. The average values given in table 1 offer useful standards, nevertheless, for recognition of anomalous concentrations of selenium in specific rock types. Some unusually high selenium values for certain geologic materials in Western United States are given in table 9. Comparison of the data in table 9 with the estimated abundance for similar materials in table 1 reveals marked enrichment of selenium in some of the tuffs, shales, limestones, sandstones, and soils of Western United States. Thus the tuffs described by Beath and others (16) as containing a maximum of 187 p.p.m. of selenium are enriched by a factor of 2,000 in comparison with Goldschmidt's average of 0.09 for the lithosphere. Similarly, concentrations of selenium have been found in shales and limestones 260 and 300 times, respectively, the average values of Rankama and Sahama; and in soils, 14,000 times Vinogradov's values. (See table 1.)

Special attention has been given to Cretaceous formations because of the early observations by Byers and because of the large area of farmlands on which soils were derived from these formations. Many soils in the plains extending eastward from the Rocky Mountains to the eastern borders of North Dakota, South Dakota, and Nebraska, to the middle of Kansas, and to the eastern border of New Mexico, as well as soils comprising many

thousands of acres of range and irrigated land in northwestern New Mexico, western Colorado, and Utah, are derived from Cretaceous sedimentary rocks. Because of the agricultural importance of these sedimentary rocks and the relative abundance of data on them, the formations of the Cretaceous period will be considered first and at greatest length, in the discussion that follows, and will be followed by a discussion of the data available on the rest of the geologic column.

## SEDIMENTARY ROCKS OF CRETACEOUS AGE

During the Cretaceous period an inland sea invaded the western plains from the Gulf of Mexico northward into Canada; it covered an area bounded roughly by the present position of the Mississippi River on the east and the eastern borders of Nevada and Idaho on the west (Eardley, 46). Sediments accumulated in this inland sea for 55 million years and later became the chalks, shales, and sandstones that are the parent materials of many soils in the same region today.

Moxon and his associates have published the most data on the selenium content of Cretaceous formations, but their data are restricted to South Dakota. Beath and his associates, who relied almost wholly on the occurrence of selenium indicator plants to evaluate the seleniferous nature of the geologic formations on which plants grow, have published a moderate amount of data on the selenium content of Cretaceous formations. Byers and his coworkers have published data on numerous random samples of Cretaceous sedimentary rocks from 10 Western States and from the eastern coast in New Jersey and Maryland. Because the results of the work of these people are scattered through many State and Federal publications and in journals of scientific societies, it is

TABLE 9.—*Some anomalously high selenium contents in materials from Western United States*

Sample No.	Material	Location	Reference	Se content
Bed No. 2	Tuffs of Eocene age	Fremont County, Wyo.	Beath and others (16)	<i>P.p.m.</i> 187
-----	do.	do.	Everett and Bauerle (51)	890
B-3321	Pierre shale, Cretaceous age	Boyd County, Nebr.	Byers (23)	103
B-18344	Shale, Niobrara formation	Pueblo County, Colo.	Byers and others (27)	156
-----	Phosphate rock in the Phosphoria formation, Permian age.	Lincoln County, Wyo.	Beath and others (13)	212
4	Vanadiferous siltstone, Phosphoria formation, Permian age.	Lincoln County, Wyo.	Beath and others (16)	680
-----	Bentonite, Niobrara formation, Cretaceous age.	Ziebach County, S. Dak.	Moxon and others (130)	113
B-3075	Chalk, Niobrara formation	Custer County, S. Dak.	Byers (23)	30
-----	Sandstone, Tertiary age	Carbon County, Wyo.	Beath and others (16)	112
B-16689	Surface soil, depth 0-6 inches	Logan County, Kans.	Byers (24)	140
B-19650	Soil, depth 26-32 inches	Fremont County, Colo.	Byers and others (27)	98

considered desirable by the author to compile these data for easy reference and access; the compilation is given in tables 10 through 14.

Table 10 gives the data available on sections of the Pierre, Niobrara, Carlile, and Greenhorn formations. The data on the Cretaceous formations and discussion of these data are presented in a sequence from youngest to oldest, contrary to common usage, because the youngest formations, the Pierre and the Niobrara, are the most seleniferous and are the parent materials of soils over vast areas of agricultural importance. The weighted average of the last column of table 10 was obtained by applying the following equation to the data:

$$\text{Weighted average} = \frac{\text{Parts per million Se} \times \text{thickness represented by each composite}}{\text{Thickness of measured section}}$$

The thickness of the section examined in most cases does not represent the thickness of the member or formation.

A correlation chart of the Cretaceous rocks discussed here is given in figure 3. This chart is particularly helpful in comparing data in table 11 with those in table 10.

Only a few Cretaceous formations have been studied, and even for these, detailed studies of the selenium content are scanty (see tables 10 and 13); thus, broad generalizations about the selenium content of the Cretaceous sedimentary rocks of Western United States are not warranted from the data available. One can conclude, however, that parts of the Niobrara and Pierre formations are locally unusually seleniferous. These seleniferous parts are potential parent materials of exceptionally seleniferous soils.

The bulk of the data available on measured sections is on the Pierre shale and is largely from the work of Moxon and his associates. In South Dakota, six members of the Pierre shale are recognized, according to Moxon and others (128). These, youngest to oldest, are Elk Butte, Mobridge, Virgin Creek, Sully, Gregory, and Sharon Springs.

No data are available on the selenium content of the Elk Butte member.

The weighted average selenium content of the Mobridge member ranges from 0.2 p.p.m. selenium in a 70-foot section in Pennington County, S. Dak., to 20.9 in a 50-foot section in Boyd County, Nebr. Moxon and others (128) pointed out that the selenium content of the Mobridge is highest in the southeastern exposures along the Missouri River near the South Dakota-Nebraska State line and that it decreases westward and northward. They stated, in this connection, that selenium in unusual quantities seems to be associated with calcareous sediments. H. A. Tourtelot, geologist, U.S. Geological Survey, who is engaged in geochemical investigations of the Pierre shale (oral communication, 1960), considers that

the Mobridge, which he has identified as a marl along the Missouri River where it is high in selenium, grades into a shale to the westward, where it is low in selenium. Within very small areas, the Mobridge member is the parent material of very seleniferous soils; but it is important to note that many soils derived from the Mobridge are practically nonseleniferous. Numerous illustrations of this variation in selenium content both within formations and in the soils derived from them are in the literature.

The weighted average selenium content of the Virgin Creek member of the Pierre shale ranges from 0.9 p.p.m. in a section 140 feet thick in Dewey County, S. Dak., to a maximum of 22.7 p.p.m. selenium in a section 25 feet thick in Gregory County, S. Dak. The same geographic trend in the distribution of selenium is shown by the Virgin Creek member as that shown by the Mobridge member.

The Sully member of the Pierre, which is 486 feet thick at the Irish Creek Well in Ziebach County, S. Dak. (Moxon and others, 130), is generally low in selenium. Its content is 0.5 p.p.m. selenium in a 100-foot section in Dewey County, S. Dak., 1.3 in the Irish Creek Well section, and 2.3 in a 20-foot section in Stanley County, S. Dak.

The data compiled on the Sharon Springs member show it to be the most uniformly seleniferous of the members of the Pierre shale, and yet the data also demonstrate the great variation in selenium content common both areally and vertically within single members of the Pierre. To illustrate: In Butte County, S. Dak., only 1 of 4 composite samples representing a 35-foot section gave a positive test for selenium; but 6 composite samples representing a 235-foot section in Ziebach County, S. Dak., ranged from 4.5 to 18 p.p.m. and gave an average value of 11.6 p.p.m. selenium.

The Niobrara formation, which directly underlies the Pierre shale (fig. 3), occurs in Nebraska, South Dakota, North Dakota, central and southeastern Montana, eastern Wyoming, eastern Colorado, northeastern New Mexico, Kansas, and southern Minnesota. The upper part is a lead-gray calcareous marl, called the Smoky Hill member, that weathers to yellowish chalk; the lower part is a medium-gray limestone called the Fort Hays limestone member. Although the Niobrara formation is of great areal extent, the areas in which it crops out to form the parent material of soils are relatively small.

The Smoky Hill member of the Niobrara is seleniferous, like the overlying Sharon Springs member of the Pierre shale. Composite samples of a 100-foot section, collected in Butte County, S. Dak., averaged 5.4 p.p.m. selenium and contained one 10-foot composite that gave no test for selenium. In this same region the Sharon Springs member of the Pierre shale also is low in selenium.

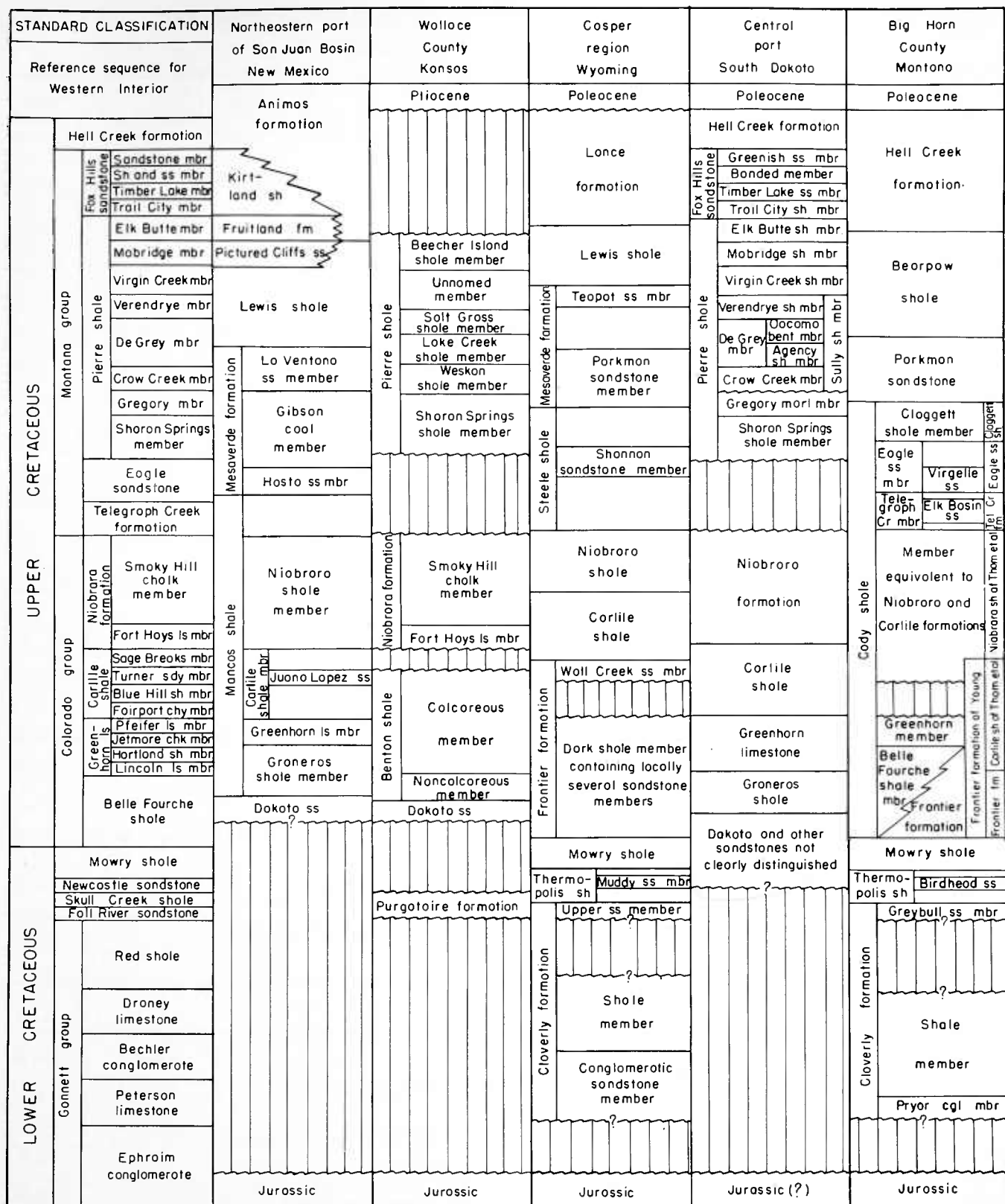


TABLE 10.—*Selenium content of sections of some sedimentary rocks of Cretaceous age*

## PIERRE SHALE-MOBRIDGE MEMBER

Location	Reference	Thick- ness	Com- posite samples	Se range	Weight- ed average
NE¼ sec. 31, T. 2 N., R. 13 E., Pennington County, S. Dak.	Moxon and others (128)----	Feet 70	Number 7	P.p.m. 0-1. 2	P.p.m. 0. 2
NE¼ sec. 16, T. 1 S., R. 19 E., Jackson County, S. Dak.	-----do-----	157	18	0-1. 0	. 3
NE¼ sec. 16, T. 1 S., R. 19 E., Jackson County, S. Dak.	-----do-----	35	4	0-1. 5	. 5
Center sec. 7, T. 1 S., R. 30 E., Jackson County, S. Dak.	-----do-----	38	4	0-1. 5	. 8
Secs. 13 and 14, T. 5 N., R. 21 E., Haakon County, S. Dak.	-----do-----	135	14	0-8. 5	. 8
Irish Creek well, SE¼ sec. 17, T. 15 N., R. 20 E., Ziebach County, S. Dak.	Moxon and others (130)----	334. 5	12	0-5. 0	. 95
NW¼NE¼ sec. 33, T. 3 N., R. 31 E., Stanley County, S. Dak.	Moxon and others (128)----	25	3	0-1. 8	. 9
Hill north of Midland, U.S. Highway No. 14, Haakon County, S. Dak.	Moxon and others (130)----	15	1	-----	1. 0
NW¼ sec. 3, T. 10 S., R. 9 E., Fall River County, S. Dak.	Moxon and others (128)----	40	4	0. 6-1. 6	1. 0
Sec. 29, T. 18 N., R. 30 E., Corson County, S. Dak.	-----do-----	120	12	0-3. 0	1. 1
1.8 mi. south of junction of U.S. Highway No. 14 and S. Dak. Highway No. 63 on U.S. 14, Stanley County, S. Dak.	Moxon and others (130)----	70	4	0-2. 3	1. 24
Sec. 2, T. 107 N., R. 78 W., Lyman County, S. Dak.	Moxon and others (128)----	72	7	0-3. 0	1. 3
Roadcut, 8 mi. east of Stamford on U.S. 16, Jones County, S. Dak.	Moxon and others (130)----	5	1	-----	1. 5
½ mi. west of junction, U.S. Highway No. 16, U.S. Highways Nos. 16 and 83, on U.S. 16, Jones County, S. Dak.	-----do-----	10	1	-----	3. 0
SE¼NE¼ sec. 29, T. 3 N., R. 31 E., Stanley County, S. Dak.	Moxon and others (128)----	60	6	1. 5-5. 0	3. 3
Sec. 17, T. 100 N., R. 72 W., Gregory County, S. Dak.	-----do-----	52	5	1. 2-10. 0	4. 2
NE¼NW¼ sec. 15, T. 106 N., R. 76 W., Lyman County, S. Dak.	-----do-----	15	3	1. 8-10. 0	5. 8
Sec. 22, T. 100 N., R. 72 W., Gregory County, S. Dak.	-----do-----	90	9	2. 0-17. 0	9. 2
Sec. 30, T. 33 N., R. 11 W., Boyd County, Nebr.	-----do-----	105	11	1. 3-40. 0	15. 1
High bare hill, sec. 3, T. 96 N., R. 67 W., Gregory County, S. Dak.	Moxon and others (130)----	90	6	10. 0-23. 0	18. 5
Sec. 33, T. 98 N., R. 68 W., Charles Mix County, S. Dak.	Moxon and others (128)----	68	7	2. 1-32. 5	20. 4
Sec. 30, T. 33 N., R. 11 W., Boyd County, Nebr. portion of zone D (iden. as Mobridge by Searight).	Byers (23)-----	50	27	1. 5-103. 0	20. 9

## PIERRE SHALE—VIRGIN CREEK MEMBER

(Type section) Sec. 29, T. 16 N., R. 29 E., Dewey County, S. Dak.	Moxon and others (128)----	140	13	0-2. 5	0. 9
Irish Creek well, SE¼ sec. 17, T. 15 N., R. 20 E., Ziebach County, S. Dak.	Moxon and others (130)----	289	4	1. 0-1. 5	1. 1
24.85 mi. west of Fort Pierre on U.S. Highway No. 14, Stanley County, S. Dak.	-----do-----	25	2	2. 0-3. 0	2. 4
Midland Hill, north of Midland, Haakon County, S. Dak.	-----do-----	10	1	-----	3. 0
Roadcut, sec. 10, T. 96 N., R. 67 W., Charles Mix County, S. Dak.	-----do-----	10	1	-----	3. 5
Sec. 22, T. 100 N., R. 72 W., Gregory County, S. Dak.	Moxon and others (128)----	25	3	6. 0-52. 0	22. 7

TABLE 10.—*Selenium content of sections of some sedimentary rocks of Cretaceous age*—Continued

## PIERRE SHALE—SULLY MEMBER

Location	Reference	Thick- ness	Com- posite samples	Se range	Weight- ed average
		<i>Feet</i>	<i>Number</i>	<i>P.p.m.</i>	<i>P.p.m.</i>
(Agency zone, Type sec.) NW¼ sec. 6, T. 12 N., R. 32 E., Dewey County, S. Dak.	Moxon and others (128)----	100	10	0-2. 1	0. 5
(Verendrye zone) sec. 36, T. 7 N., R. 17 E., Meade County, S. Dak.	-----do-----	40	4	. 5-1. 2	. 8
(Verendrye zone) Fort Pierre, Stanley County, S. Dak.	Moxon and others (130)----	78	6	0-2. 0	1. 0
Irish Creek well, SE¼ sec. 17, T. 15 N., R. 20 E., Ziebach County, S. Dak.	-----do-----	486	15	0-5. 0	1. 3
(Agency zone) Railway cut, Fort Pierre, Stanley County, S. Dak.	-----do-----	30	2	. 3-2. 0	1. 15
(Gregory zone) Oacoma Hill, Lyman County, S. Dak.	-----do-----	6	1	-----	2. 2
(Oacoma zone) Fort Pierre County, S. Dak. below Verendrye monument.	-----do-----	20	2	2. 2-2. 5	2. 3

## PIERRE SHALE—SHARON SPRINGS MEMBER

SE¼SW¼ sec. 8, T. 11 N., R. 3 E., Butte County, S. Dak.	Moxon and others (128)----	35	4	0-1. 3	0. 3
Sec. 32, T. 103 N., R. 72 E., Lyman County, S. Dak.	-----do-----	126	14	. 7-24. 0	5. 8
Sec. 23, T. 3 S., R. 8 E., Custer County, S. Dak. (Iden. as Sharon Springs by Searight).	Byers (23)-----	4. 5	6	2. 0-8. 0	7. 3
SE¼ sec. 13, T. 1 S., R. 8 E., Pennington County, S. Dak.	Moxon and others (128)----	58	6	3. 0-21. 0	8. 2
Secs. 5 and 8, T. 7 S., R. 7 E., Fall River County, S. Dak.	-----do-----	80	8	. 6-13. 0	9. 1
Irish Creek well, SE¼ sec. 17, T. 15 N., R. 20 E., Ziebach County, S. Dak.	Moxon and others (130)----	235	6	4. 5-18. 0	11. 6
N. ½ sec. 19, T. 10 S., R. 3 E., Fall River County, S. Dak.	Moxon and others (128)----	95	10	8. 5-24. 0	14. 3
Rosebud Bridge, Gregory County, S. Dak.----	Moxon and others (130)----	20	2	16. 0-21. 0	18. 5

## NIOBRARA FORMATION

SW¼ sec. 32, T. 8 S., R. 1 E., Fall River County, S. Dak.	Moxon and others (128)----	30	3	1. 6-7. 0	4. 0
SW¼ sec. 16, T. 4 S., R. 8 E., Custer County, S. Dak.	-----do-----	57	6	2. 7-16. 0	5. 7
Irish Creek well, SE¼ sec. 17, T. 15 N., R. 20 E., Ziebach County, S. Dak.	Moxon and others (130)----	270	9	10. 0-22. 0	14. 8
NW¼ sec. 26, T. 10 N., R. 2 E., 8.5 mi. north of Mobile Station at Belle Fourche, Butte County, S. Dak.	Moxon and others (128)----	25	3	16. 0-21. 0	18. 1
Sec. 17, T. 104 N., R. 71 W., railroad cut at Oacoma, west end of Missouri River bridge, Lyman County, S. Dak.	-----do-----	82	8	16. 0-45. 0	33. 5

## NIOBRARA FORMATION—SMOKY HILL MEMBER

NE¼ sec. 6, T. 8 N., R. 5 E., Butte County, S. Dak.	Moxon and others (128)----	100	10	0-8. 7	5. 4
Spillway, Lake Henry, Bon Homme County, S. Dak.	Moxon and others (130)----	5	1	-----	6. 5
8.5 mi. west of Pine Ridge, Shannon County, S. Dak.	Moxon and others (128)----	25	3	7. 0-11. 6	8. 0
SE¼ sec. 33, T. 8 S., R. 1 W., Niobrara County, Wyo.	-----do-----	120	12	. 6-24. 0	11. 8
SE¼ sec. 35, T. 1 N., R. 8 E., Pennington County, S. Dak.	-----do-----	86	9	5. 7-21. 0	12. 6

TABLE 10.—*Selenium content of sections of some sedimentary rocks of Cretaceous age—Continued*

## NIOBRARA FORMATION—SMOKY HILL MEMBER—Continued

Location	Reference	Thick- ness	Com- posite samples	Se range	Weight- ed average
SW¼SW¼, sec. 18, T. 10 S., R. 3 E., Fall River County, S. Dak.	Moxon and others (128)----	<i>Feet</i> 44	<i>Number</i> 5	<i>P.p.m.</i> 8. 0–24. 0	<i>P.p.m.</i> 15. 0
Eads, Colo.	Williams and others (208)---	80	8	8. 0–16. 0	12. 0
NE¼ sec. 17, T. 93 N., R. 56 W., Yankton County, S. Dak.	Moxon and others (130)----	90	9	2. 0–16. 0	6. 5
SE¼ sec. 31, T. 7 N., R. 6 E., Meade County, S. Dak.	Moxon and others (128)----	65	7	6. 3–27. 0	17. 0
Sec. 23, T. 3 S., R. 8 E., Custer County, S. Dak.	Byers (23)-----	34	12	6. 0–30. 0	17. 1
Railroad cut, Oacoma, Lyman County, S. Dak.	Moxon and others (130)----	25	2	24. 0–28. 0	26. 4

## NIOBRARA FORMATION—FORT HAYS MEMBER

NW¼ sec. 9, T. 93 N., R. 52 W., Clay County, S. Dak.	Moxon and others (130)----	10	1	-----	0
Spillway Lake Henry, Scotland, S. Dak.	do-----	9	1	-----	. 3
Quarry, Spirit Mound, Clay County, S. Dak.	do-----	10	1	-----	1. 0
Spirit Mound above quarry, Clay County, S. Dak.	do-----	10	1	-----	1. 5
Lake Henry Spillway, Scotland, Bon Homme County, S. Dak.	do-----	5	1	-----	3. 0

## CARLILE FORMATION

Irish Creek well, SE¼ sec. 17, T. 15 N., R. 20 E., Ziebach County, S. Dak.	Moxon and others (130)----	384	13	0. 0–3. 0	0. 84
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## GREENHORN FORMATION

Irish Creek well, SE¼ sec. 17, T. 15 N., R. 20 E., Ziebach County, S. Dak.	Moxon and others (130)----	346	15	0–6. 0	2. 2
Sec. 18, T. 22 S., R. 66 W., Pueblo County, Colo.	Byers and others (27)-----	39	32	. 1–8. 0	1. 3
SW¼ sec. 13, T. 9 S., R. 2 E., south of Edgemont, Fall River County, S. Dak.	Moxon and others (128)----	44	5	0–3. 2	1. 6
NE¼ sec. 27, T. 9 N., R. 2 E., Butte County, S. Dak. (Se content was reported as 0.0 Se p.p.m. for 7 of these 10-ft composite samples.)	do-----	110	11	. 1–1. 0	. 2

content. A remarkably uniform 25-foot section of the Smoky Hill member from Lyman County, S. Dak., contained 26 p.p.m. selenium. Some seleniferous soils are derived from the Smoky Hill member of the Niobrara in eastern Colorado, southwestern Kansas, eastern Wyoming, northwestern Nebraska, southwestern South Dakota, and adjacent to the Missouri River in the southern portion of South Dakota and northeastern Nebraska.

Only a few samples of the Fort Hays member of the Niobrara formation were analyzed by Moxon and others (130), and they were found to contain little selenium. The highest value reported is 3 p.p.m. for a 5-foot composite sample in Bon Homme County, S. Dak.

The Carlile formation, underlying the Niobrara formation in South Dakota, is notably low in selenium content. In western South Dakota it is a medium- to dark-gray noncalcareous shale that is slightly sandy in places (Moxon and others, 130). The highest selenium content found in 13 composite samples representing its entire thickness of 384 feet was 3 p.p.m.; two of these composites contained no selenium, and the weighted average selenium content for the formation was 0.84.

The Greenhorn formation, which underlies the Carlile formation, occurs in eastern Colorado and Wyoming, northeastern New Mexico, southeastern Montana, Nebraska, South Dakota, and Kansas, and consists of beds of chalk, shale, and lime-

stone. A 346-foot section at Irish Creek Well in Ziebach County, S. Dak., averaged 2.2 p.p.m. selenium. Samples of 60 feet of this section contained no detectable amount of selenium; one composite of 23 feet contained only 0.8; the remaining 12 composites ranged from 1 to 6 p.p.m. Moxon and others (128) were of the opinion "that the selenium content of the Greenhorn formation in South Dakota is so low that toxic soils are not likely to be developed from it." Selenium-indicator plants found growing on the formation were of relatively low selenium content. Byers and others (27) report 32 composite samples representing a section 39 feet thick in Pueblo County,

Colo., contained 0.1 to 8 p.p.m. selenium with a weighted average of 1.3. Byers stated that these values for the Greenhorn are about the same as his unpublished values for the upper portions of the Pierre shale in South Dakota and for the upper portions of the Mancos shale in western Colorado.

In table 11 are listed grab samples of various Cretaceous formations from nine Western States. The interpretative value of these samples is limited because of their inadequate number and the fact that, except for the North Dakota samples, the stratigraphic position within the formation is unknown.

TABLE 11.—*Selenium content of grab samples from some sedimentary rocks of Cretaceous age*

COLORADO

Sample No.	Location	Formation or member	Reference	Se
				<i>P.p.m.</i>
B-11382	14 mi. north of Fort Morgan, Morgan County	Pierre	Byers (23)	0
B-11383	9 mi. north of Fort Morgan, Morgan County	do	do	.5
B-11380	12 mi. north of Sterling, Logan County	do	do	0
B-11381	9 mi. north of Sterling, Logan County	do	do	2.0
B-11397	19 mi. south of Fort Morgan, Adams County	do	do	.2
B-11399	23¼ mi. south of Fort Morgan, Adams County	do	do	.5
B-18361	38 mi. south of Pueblo, Huérfino County	do	Byers and others (27)	.8
B-18123	½ mi. south of Haswell, Kiowa County	Niobrara	do	54.0
B-18342	1 mi. west of Pueblo—U.S. Highway No. 150, Pueblo County	do	do	3.5
B-18344	3 mi. west of Pueblo, Pueblo County	do	do	156.0
B-11415	3 mi. south of Ayer, Otero County	do	Byers (23)	.5
B-15103	3 mi. north of Whitewater, Mesa County	Mancos	Byers (24)	3.0
B-15065	8 mi. north of Delta, Delta County	do	do	2.0

KANSAS

B-16523	Sec. 32, T. 13 S., R. 36 W., Logan County, at contact with Ogallala.	Pierre	Byers (24)	6.0
B-5298	Sec. 11, T. 13 S., R. 42 W., Wallace County	Weskan	Byers (23)	.5
B-16176	Center of sec. 13, T. 12 S., R. 37 W., Logan County	Pierre	Byers (24)	10.0
B-16177	Center of sec. 13, T. 12 S., R. 37 W., Logan County	do	do	22.0
B-16892	Sec. 1, T. 14 S., R. 35 W., Logan County	Niobrara	do	18.0
B-16697	Sec. 28, T. 14 S., R. 31 W., Grove County	do	do	18.0
B-16184	SE corner, sec. 24, T. 13 S., R. 37 W., Logan County	Smoky Hill	do	16.0
B-16191	NE corner, sec. 1, T. 15 S., R. 37 W., Logan County	do	do	8.0
B-16696A	SE ¼, sec. 21, T. 13 S., R. 35 W., Logan County	do	do	22.0
B-17367	Sec. 29, T. 8 S., R. 20 W., Rooks County	do	do	8.0
B-16718	East of Trego Center, Trego County	Fort Hays	do	.5
B-17128	Sec. 10, T. 15 S., R. 24 W., Trego County	do	do	.3
B-17434	Sec. 13, T. 10 S., R. 17 W., Rooks County	do	do	6.0
B-17166	Sec. 2, T. 15 S., R. 22 W., Trego County	Carlile	do	.7
B-17177	Sec. 8, T. 15 S., R. 21 W., Trego County	do	do	.5
B-5271	4 mi. south of Belvedere, Comanche County	Kiowa	Byers (23)	1.5

MONTANA

B-15447	2 mi. northeast of Nashua, Valley County	Bearpaw	Byers (24)	2.0
B-15505	3 mi. north of Leedy, Phillips County	do	do	2.0
B-15503	6½ mi. north of Leedy, Phillips County	do	do	2.0
B-15531	5 mi. west and 2.4 north of Phillips, Phillips County	do	do	1.0
B-15533	5 mi. west and ¼ mi. north of Phillips, Phillips County	do	do	1.5

TABLE 11.—*Selenium content of grab samples from some sedimentary rocks of Cretaceous age—Con.*

## MONTANA—Continued

Sample No.	Location	Formation or member	Reference	Se
B-15535-----	6.3 mi. south of Brookside, Phillips County-----	Bearpaw-----	Byers (24)-----	2.0
B-15540-----	24 mi. north of Dodson, Phillips County-----	do-----	do-----	.8
B-15459-----	4 mi. northeast of Cottonwood Creek Bridge, Phillips County.	Judith River-----	do-----	1.5
B-15466-----	Cottonwood Creek Bridge, Phillips County-----	Claggett-----	do-----	2.0
B-15509-----	6 mi. west of Leedy, Phillips County-----	do-----	do-----	.8
B-15678-----	11.4 mi. east of Ethridge, Toole County-----	Colorado-----	do-----	1.5
B-15682-----	1.8 mi. north of Shelby, Toole County-----	do-----	do-----	2.0
B-6295-----	18 mi. east of Ridge, Carter County-----	Graneros-----	Byers (23)-----	.5

## NEBRASKA

II

B-4374-----	Sec. 2, T. 1 N., R. 17 W., Harlan County-----	Pierre-----	Byers (23)-----	8.0
B-4375-----	Sec. 21, T. 1 N., R. 17 W., Harlan County-----	do-----	do-----	31.0
B-7745-----	Sec. 17, T. 1 N., R. 17 W., Harlan County-----	do-----	do-----	20.0
B-7746-----	At bridge south of Alma, Harlan County-----	do-----	do-----	7.0
B-7750-----	Sec. 3, T. 1 N., R. 37 W., Dundy County-----	do-----	do-----	3.5
B-14619-----	Southwest corner, sec. 13, T. 33 N., R. 52 W., Dawes County, 15-ft. composite.	do-----	Byers (24)-----	1.5
B-14680-----	Sec. 22, T. 35 N., R. 47 W., Dawes County-----	do-----	do-----	10.0
B-7739-----	Sec. 16, T. 1 N., R. 9 W., Webster County-----	Niobrara-----	Byers (23)-----	8.0
B-7741-----	Sec. 2, T. 1 N., R. 11 W., Webster County-----	do-----	do-----	9.0
B-7742-----	1 mi. west of Riverton, Franklin County-----	do-----	do-----	10.0
B-7743-----	Sec. 5, T. 1 N., R. 14 W., Franklin County-----	do-----	do-----	11.0
B-7747-----	Sec. 23, T. 2 N., R. 21 W., Furnas County-----	do-----	do-----	6.0
B-4373-----	Sec. 15, T. 1 N., R. 17 W., Harlan County-----	do-----	do-----	20.0
B-14673-----	Sec. 28, T. 35 N., R. 47 W., Dawes County-----	Carlile-----	Byers (24)-----	.5
B-14672-----	Sec. 34, T. 35 N., R. 47 W., Dawes County-----	Graneros-----	do-----	.5

## NEW MEXICO

B-18150-----	On U.S. Highway No. 85 at Raton-----	Pierre-----	Byers and others (27).	0.8
B-20251-----	2 mi. northwest of Colfax, T. 28 N., R. 21 E., Colfax County.	do-----	do-----	1.0

## NORTH DAKOTA

B-26420-----	Workings of former Northern Cement & Plaster Co., on Olson farm, 2 mi. Southwest of Concrete, Cavalier County, N. Dak.; bentonite 4 ft. above limonite layer at contact of Pierre and Niobrara formations.	Pierre-----	Lakin and Byers (102).	1.6
B-26421-----	Same as above, fissile shale immediately above limonite layer at contact of Pierre and Niobrara formations.	do-----	do-----	32.0
B-26422-----	Same as above, limonite layer at contact of Pierre and Niobrara formations.	do-----	do-----	34.0
B-26423-----	Same as above, nodule in Niobrara 6 inches below limonite layer at contact of Pierre and Niobrara formations.	Niobrara-----	do-----	36.0
B-26424-----	Same as above, "cement rock," 5 ft. below limonite layer at contact of Pierre and Niobrara formations.	do-----	do-----	14.0
B-26425-----	Same as above, yellow seam 3 inches thick immediately below "cement rock."	do-----	do-----	28.0

## SOUTH DAKOTA

B-15157-----	Sec. 4, T. 8 S., R. 6 E., Shannon County 10-ft. composite-----	Graneros-----	Byers (24)-----	0.7
B-15155-----	Sec. 33, T. 7 S., R. 6 E., Shannon County 10-ft. composite-----	do-----	do-----	1.5



TABLE 11.—*Selenium content of grab samples from some sedimentary rocks of Cretaceous age—Con.*

## UTAH

Sample No.	Location	Formation or member	Reference	Se
B-12137	1 mi. east of Jensen	Mancos	Byers (23)	5.0
B-12135	5 mi. east of Jensen	do.	do.	3.0
B-12539	6 mi. west of Cisco	do.	do.	8.0
B-12520	1½ mi. west of Desert Switch	do.	do.	.2

## WYOMING

B-4834	Sec. 16, T. 16 N., R. 74 W., Albany County	Steele	Byers (23)	6.0
B-4831	Sec. 16, T. 16 N., R. 74 W., Albany County	Niobrara	do.	4.0
B-5668	Sec. 16, T. 27 N., R. 76 W., Albany County	do.	do.	55.0
B-6317	3½ mi. southeast of Upton, Weston County	Graneros	Byers (24)	1.0
B-4801	Sec. 21, T. 14 N., R. 74 W., Albany County	Benton	Byers (23)	1.0

The Pierre shale in Kansas, as represented by three samples, appears to be erratically seleniferous. The Smoky Hill member of the Niobrara is seleniferous in Kansas, at least in part; however, the underlying Fort Hays limestone member is relatively free of selenium. The samples of the Pierre and Niobrara formations collected in Nebraska range from 1.5 to 30 p.p.m. Very little selenium was found in the Pierre formation in Colorado; the Niobrara formation seems to be very seleniferous, but perhaps the highly seleniferous areas are small and local. In Wyoming the Niobrara formation and the Steele formation, which is partly equivalent to the Pierre, are also variably seleniferous. Six samples collected near the contact of the Pierre and Niobrara formations in northeastern North Dakota contain from 1.6 to 36 p.p.m. of selenium; this is about the same range as that found in these formations in South Dakota, Wyoming, and Kansas. In contrast, the Cretaceous shales that have been sampled in Montana are low in selenium content; the maximum was 2 p.p.m. The two samples from the Pierre shale in New Mexico are likewise low.

The Niobrara formation and lower part of the Pierre shale found east of the Rocky Mountains are correlated with the upper part of the Mancos shale west of these mountains (see fig. 3). The Mancos shale occurs in western Colorado, northwestern New Mexico, eastern Utah, and southern and central Wyoming; it ranges in thickness from 1,200 to 2,500 feet. Soils derived from the Mancos shale cover large areas in eastern Utah and western Colorado. Neither the Mancos shale nor the soils derived from it have been studied sufficiently

to evaluate either the existence or extent of seleniferous beds within the formation, or the selenium content of the soils derived from these beds. The six samples of Mancos shale that have been analyzed for selenium—four in Utah and two in Colorado—contained 0.2 to 8.0 p.p.m. Trelease and Beath (185) reported the collection of 17 selenium-indicator plants growing on Mancos shale in Utah; the plants contained 54 to 2,210 p.p.m. selenium; 13 seleniferous plants growing on the Mancos in New Mexico contained 84 to 1,640; and 26 selenium-indicator plants growing on the Mancos in Colorado contained 65 to 2,148 p.p.m. Some soils in Mesa, Montrose, and Delta Counties, Colo., derived in part from Mancos shale, were reported by Byers (24) to contain 0.2 to 10 p.p.m. selenium.

The data available on the selenium content of the Graneros, Benton, and Carlile formations are inadequate. The few available analyses range from 0.5 to 7.0 p.p.m. selenium.

Samples of Cretaceous shales were collected by Lakin and Byers (101) at outcrops from the coastal bluffs near Los Angeles and northward, for approximately 400 miles, to the vicinity of Maxwell, Colusa County, Calif. Part of the data obtained in this reconnaissance is given in table 12; the selenium content of these samples ranged from 0.1 to 25.0 p.p.m. These results contrast strongly with those obtained on Cretaceous materials collected along the eastern coast of the United States (table 13). The 28 samples of eastern materials range in selenium content from 0 to 5 p.p.m.; only 3 contained as much as 1 p.p.m. selenium.

TABLE 12.—*Selenium content of some Cretaceous shales in California*<sup>1</sup>

Sample No.	Location	Se
B-25440	2 mi. north of Santa Monica on U.S. Highway No. 101A, Los Angeles County.	<i>P.p.m.</i> 18.0
B-25441	do	22.0
B-25444	2 mi. west of Junction with route 27 on U.S. Highway No. 101A, at base of bluff above beach, Los Angeles County.	24.0
B-25453	2½ mi. up La Brea Creek from Spanish ranch, Santa Barbara County.	1.0
B-25472	2 mi. west of Pozo on route 178, San Luis Obispo County.	.2
B-25474	6.3 mi. west of Pozo on route 178, San Luis Obispo County.	.2
B-25475	8.2 mi. west of Pozo on route 178, San Luis Obispo County.	1.0
B-25479	5.5 mi. northeast of Cholame, San Luis Obispo County.	.1
B-25480	do	1.0
B-25488	1½ mi. east of Kern County line on route 41, Kern County.	.2
B-25545	15 mi. south of Tracy on Hospital Creek, San Joaquin County.	5.0
B-25547	14½ mi. south of Tracy on Hospital Creek, San Joaquin County.	8.0
B-25548	100 yds. from sample B-25547	2.0
B-25550	do	28.0
B-25584	10 mi. southwest of Williams on route 20, Colusa County.	.2
B-25590	7 mi. west of Maxwell, up Coral Creek canyon, Colusa County.	6.0

<sup>1</sup> Data from Lakin and Byers (101).TABLE 13.—*Selenium content of some Cretaceous rocks in eastern United States*<sup>1</sup>

Sample No.	Location	Se
B-25998	0.7 mi. east of White Horse, Raritan formation, Mercer County, N.J.	<i>P.p.m.</i> 0.4
B-25999	do	.2
B-26005	0.5 mi. west Crosswicks, Woodbury formation, Burlington County, N.J.	.6
B-26006	Highway intersection Kinkora, Merchantville formation, Burlington County, N.J.	.8
B-26007	1 mi. southwest of Morristown, red sand, Englishtown formation, Burlington County, N.J.	.1
B-26008	1 mi. southwest of Morristown, yellow and gray sand, Englishtown formation, Burlington County, N.J.	.04
B-26029	Permutit Co. pit, Burmingham, green sand, Hornerstown formation, Burlington County, N.J.	2.4

TABLE 13.—*Selenium content of some Cretaceous rocks in eastern United States*<sup>1</sup>—Continued

Sample No.	Location	Se
B-26023	0.5 mi. north of Crawford's Corner, green sand, Hornerstown marl, Monmouth County, N.J.	<i>P.p.m.</i> 0.4
B-26028	0.25 mi. west of railroad station at Highlands, green sand, Navesink marl, Monmouth County, N.J.	.6
B-25921	Orloff sand pit, District of Columbia, top portion of Magothy formation.	.2
B-25922	Orloff sand pit, District of Columbia, Magothy formation, 12 ft. above base.	.2
B-25923	Orloff sand pit, District of Columbia, probably basal Monmouth formation.	.8
B-25924	Orloff sand pit, District of Columbia, undoubtedly Monmouth formation.	1.0
B-25925	Branch Ave., just east of District line, District of Columbia, Monmouth formation.	.6
B-25927	On Crystal Springs Ave., 300 yd. south of Central Ave. in Seat Pleasant, Md., top of Potomac formation.	.2
B-25948	On Crystal Springs Ave., 300 yd. south of Central Ave. in Seat Pleasant, Md., variegated red-yellow-gray clay.	.2
B-25928	On Benning Road, ¼ mi. southeast of District Line, clay from Potomac formation.	.5
B-25947	On Benning Road, ¼ mi. southeast of District Line, ferruginous concretion, Potomac series.	.6
B-25929	do	.3
B-25930	29th and Adams Streets NE, District of Columbia, clay, Potomac series.	.5
B-25949	29th and Adams Streets NE, District of Columbia, red clay.	.1
B-25950	29th and Adams Streets NE, District of Columbia, iron concretion.	0
B-25951	29th and Adams Streets NE, District of Columbia, pyrite and lignite.	0
B-25952	29th and Adams Streets NE, District of Columbia, iron concretion.	.1
B-25931	Daniels sand pit, Mount Rainier, Md., lenticular mass of sand, Potomac series.	.7
B-25932	Daniels sand pit, Mount Rainier, Md., purple and pink concretions.	5.0
B-25953	do	.8
B-25933	Piney Branch Road and Ray Road, Takoma Park, Md., sandy clay, Patuxent.	.7

<sup>1</sup> Data from Lakin and Byers (101).

## ROCKS AND SEDIMENTS OF VARIOUS AGES

Less is known about the selenium content of rocks of other geologic periods than about the selenium content of Cretaceous rocks. Part of the data available is given in table 14. These rocks and sediments are described in order of increasing age. The Manning Canyon shale of Mississippian and Pennsylvanian age, the Phosphoria formation of Permian age, and certain tuffs of Tertiary age are noticeably high in selenium.

The glacial tills of northeastern South Dakota contain appreciable amounts of selenium, undoubtedly because of the relatively seleniferous Cretaceous beds from which they are derived in part. According to Searight and others (163), selenium is leached from these Pleistocene deposits, transported downslope, and deposited at lower levels. Maximum amounts of selenium in these enriched areas are about the same as the average amounts of selenium in toxic soils (toxic soils, as here used, are those that produce seleniferous vegetation toxic to animals) derived directly from Cretaceous formations. Lakin and Byers (102) reported a similar system of leaching of till and enrichment in lacustrine beds in North Dakota. Local enrichment by deposition from ground waters probably has occurred in widely differing times and areas.

The selenium content in the rest of the material listed in table 14 differs little from the average for the rock types, as shown in table 1.

In addition to these data, indirect evidence of the presence of seleniferous rocks is given by the growth of seleniferous vegetation on soils derived from the rocks. Trelease and Beath (185) reported finding seleniferous plants growing on 55 formations in 15 Western States, but very seldom confirmed the seleniferous character of these formations by analysis. The formations range in age from Pennsylvanian through Quaternary; 22, however, are of Cretaceous age.

The presence of appreciable amounts of selenium in the uranium deposits of the Colorado Plateau is often indicated by the growth of selenium-indicator plants over the ore. Helen L. Cannon (30, 31) and Cannon and Kleinhampl (32) have developed a useful method of prospecting for uranium based on the distribution of selenium-indicator plants.

## DISCUSSION

The selenium content of samples of sedimentary rocks in the Western United States ranges from less than 0.02 p.p.m. to more than 1,500 p.p.m. Individual formations vary in selenium content between wide limits, both vertically and areally.

TABLE 14.—*Selenium content of some non-Cretaceous rocks and sediments in western United States*

Period	Formation	Reference	Location	Samples	Se range
Quaternary	De Smet till	Searight and Moxon (164).	South Dakota	Number 23	P.p.m. 0. 27-5. 38
Do	Mankato till	do	do	1	. 86
Do	Arlington glacial till	do	do	104	. 2-4. 92
Do	Kansan and Iowan till	do	do	13	. 31-3. 7
Tertiary	Brule shale	Byers (24)	Nebraska	1	. 2
Do	Bridger shale	Byers (23)	Wyoming	2	. 4- 8
Do	Eocene tuffs	Everett and Bauerle (51).	Lysite, Wyo.	245	40. 0-1, 000. 0
Do	do	do	do	<sup>1</sup> 1	160. 0
Do	do	Beath and others (16)	Wyoming	5	12. 5-187. 0
Do	do	Beath and others (11)	do	1	. 32
Jurassic	Morrison	Byers (23)	South Dakota	3	0-4. 8
Do	do	Knight and Beath (97)	Wyoming	1	. 23
Do	Gunnison	Byers (24)	Colorado	1	5. 0
Triassic	Spearfish	Byers (23)	South Dakota	1	1. 0
Do	Dinwoody	Beath and others (13)	Wyoming	<sup>1</sup> 1	1. 0
Permian	Phosphoria	do	do	39	. 8-2. 2
Do	do	Beath and others (16)	do	11	188. 0-680. 0
Pennsylvanian and Mississippian.	Manning Canyon shale	Beath and others (14)	Utah	20	. 4-96. 0
Do	do	Lakin and Byers (102)	do	7	. 4-54. 0
Mississippian	Great Blue limestone	do	do	1	1. 2
Do	Pahasapa limestone	Moxon and others (128)	South Dakota	1	. 25
Ordovician	Whitewood limestone	do	do	1	. 8

<sup>1</sup> Composite sample.

Certain formations, however, contain abnormal amounts of selenium (greater than 2 p.p.m.) throughout large portions of their stratigraphic thickness over large areas. Certain zones in the Manning Canyon shale and Phosphoria formation of Paleozoic age contain 100 to 600 times as much selenium as the average of the 36 European Paleozoic shales reported by Minami (121). The Niobrara and Pierre formations of Mesozoic age also contain much selenium, but the selenium content of samples ranges from less than 0.1 to more than 100 p.p.m. and is erratically distributed vertically. A high selenium content is characteristic of the rocks of the upper part of the Niobrara and the lower part of the Pierre; an average of 20 p.p.m. was found above and below the contact of these two formations in northeastern North Dakota, northeastern Nebraska, and west-central Kansas. Some extremely seleniferous tuffs of Cenozoic age occur in Wyoming, containing as much as 187 p.p.m. selenium, much of which is water soluble according to Beath and others (16).

Numerous accounts in the literature describe areas where selenium has been concentrated lo-

cally by precipitation from seleniferous waters. One can expect that after ancient seleniferous beds have been eroded away, local concentrations will form again in resultant younger beds. Sediments high in selenium have existed in Western United States ever since the Manning Canyon shale was laid down approximately 250 million years ago. Thus, it is not surprising that Trelease and Beath (185) have found seleniferous plants growing on 55 different sedimentary formations in Western United States.

The seleniferous soils of the Great Plains region in Montana, North Dakota, South Dakota, Wyoming, Nebraska, Kansas, and Colorado are derived primarily from sedimentary rocks of Late Cretaceous age. The rocks of the formations are horizontal throughout the area and are extremely variable in selenium vertically. Such variation in parent material makes possible a wide range of the selenium content of the soils in a single field. Thus, in gently rolling topography the wide range in selenium content of the parent material gives rise to relatively large areas of mildly seleniferous soils spotted with small markedly seleniferous areas.

## Chemical Determinations of Selenium

By M. S. ANDERSON

Precise methods for the determination of selenium are basic for investigations of this element in agriculture. Qualitative methods for the determination of selenium have been available for a long time. Quantitative methods have also been used, but their precision was not adequate for a study of the small quantities often present in potentially dangerous vegetation. Even smaller quantities must also frequently be determined in soils. The quantities present in these materials are best expressed as parts per million. In water and in a few other materials where the quantities present are normally very small, the results are expressed as parts per billion. The methods used must of necessity be highly sensitive.

### OLD METHODS

An analytical procedure found in older textbooks of quantitative chemical analysis calls for fusion with sodium carbonate and potassium nitrate. The resulting alkali selenate that is soluble in water is dissolved and acidified with hydrochloric acid. The selenium is then precipitated with hydrazine hydrate.

A later method was used to some extent in the first selenium investigations at the Wyoming Agricultural Experiment Station (11, 178). This

involves treatment of dry plant tissue with sodium hydroxide solution followed by ignition at a low temperature. The residue is treated with hydrochloric acid, filtered, and the clear solution treated with hydroxylamine to reduce selenium to elemental form.

A qualitative method that was used to some extent for detection of organic selenium compounds was one devised by Horn (79). A dried sample of plant or animal material was placed in a Kjeldahl flask with 40 ml. of concentrated sulfuric acid and 0.2 gram of mercuric oxide, digested, diluted, and treated with a few drops of an aqueous solution of codeine sulfate. A green color changing to blue indicates the presence of selenium.

When it was demonstrated by the then available methods that selenium was present in such vegetation as wheat, the need for more precise and reliable analytical methods was urgent. The chemical methods must be adequately precise, flexible as to detail, and involve no great difficulty of operation.

### CURRENT METHODS

A method that meets the varied requirements of an agricultural chemist was developed by

Robinson and associates (155). The method specifies details of procedure for soils, pyrites, and other sulfides, water, vegetable matter, and animal tissue.

This method with only minor modifications has been used in the U.S. Department of Agriculture for making about 10,000 determinations. The selenium contents ranged from less than one-tenth part per million to more than 1 percent. A detailed description of the method was published by Williams (204) after it had been in use several years. The method is based on the fact that selenium tetrabromide is volatile under the conditions of distillation with hydrobromic acid and bromine, whereas tellurium is not volatile. The distillation apparatus used is shown in figure 4.

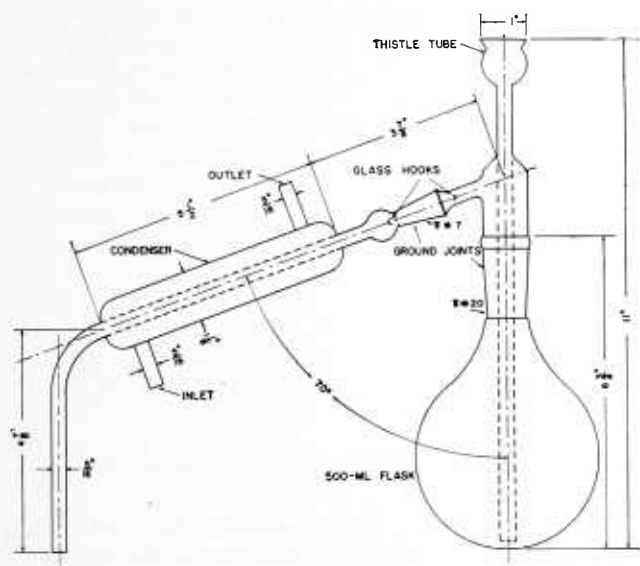


Figure 4.—Apparatus employed in the distillation procedure.

This is copied from an earlier description of the method by Robinson and associates (155).

**Distillation.**—Place 50 grams of air-dry soil that has passed a 2-mm. sieve in the distilling flask. Add to the contents of the flask, slowly and with constant shaking, 100 ml. of 48-percent HBr containing 2 to 3 ml. of  $\text{Br}_2$ .

After any frothing due to decomposition of carbonates has subsided, connect the still so that the adapter is below the surface of the 5 ml. of  $\text{Br}_2$  water in the receiving flask. [The success of the distillation depends on the saturation of the organic matter in the soil with  $\text{Br}_2$  so that it will not reduce the  $\text{SeBr}_4$  during the distillation.] Apply heat gradually. When the mixture begins to boil, adjust the flame so that the distillation proceeds very slowly (approximately 20 minutes for 1 to 2 ml. of bromine), thereby giving time for the  $\text{Br}_2$  and soil organic matter to react. If insufficient  $\text{Br}_2$  was added to the soil to give 1 to 2

ml. in the distillate, remove the flame and add more  $\text{Br}_2$  in HBr solution through the thistle tube. [After this period of bromination, the distillation may be finished rapidly.] Collect 50 to 60 ml. of distillate. To check the complete distillation of the selenium, add more HBr and  $\text{Br}_2$  to the residue and collect a second distillate. Remove the receiving flask, dilute the distillate to 80 to 90 ml. with distilled water, and pass in  $\text{SO}_2$  until the  $\text{Br}_2$  is reduced and the solution becomes essentially saturated with the  $\text{SO}_2$ . [If the reduction is made in concentrated acid and the amount of selenium is small, it often precipitates as a yellow, finely divided form that is exceedingly hard to retain on a filter mat.] Keep the solution cool during the reduction with  $\text{SO}_2$  to avoid possible loss by volatilization just as the reduction of the  $\text{Br}_2$  is completed. Add 0.3 to 0.5 gram of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) and warm on the steam bath for 10 minutes.

**Estimation.**—Set the distillate aside for 48 hours to allow complete reduction and coagulation of the selenium. Examine the distillate for selenium; if the amount is small, employ the Tyndall effect, using either direct sunlight or a strong, well-focused, artificial light. As little as 0.005 mg. may be easily seen by this method. Filter the selenium on a tight asbestos mat in a Gooch crucible, wash with cold water, then with alcohol to remove the oily material always present in soil distillates, and again wash with cold water. If the amount of selenium is 0.5 mg. or less, dissolve on the pad with 10 ml. of water-white 48-percent HBr to which has been added 3 ml. of  $\text{Br}_2$  per liter. Filter into a 25-ml. volumetric flask and wash the pad with cold water until the volume reaches 24 ml. Pass in  $\text{SO}_2$  until the solution is essentially saturated. Add 1 ml. of a fresh solution of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  containing 10 grams per 100 ml. of solution. Shake well. Heat on the steam bath for 20 minutes, bringing the temperature to  $45^\circ$  to  $50^\circ$  C. Cool to room temperature, shake well, and compare in Nessler tubes with known amounts of selenium precipitated in the same manner. Prepare fresh standards each time. [In routine work it is convenient to accumulate 25 to 50 samples for estimation.] Then prepare standards containing 0.01, 0.025, 0.05, 0.10, 0.15, 0.20, 0.30, and 0.50 mg. of selenium from a standard stock solution of  $\text{Na}_2\text{SeO}_3$  or  $\text{Na}_2\text{SeO}_4$ . [By treating each sample and the standards exactly alike in the manner described, the colored turbidities can be readily matched. Despite all precautions, an off-colored one will be obtained from time to time. Such samples must be refiltered and determined with the next set.]

If more than 0.5 mg. of selenium is present, dissolve it into a 100-ml. beaker, using 30 ml. of HBr containing 0.2 to 0.3 ml. of bromine, and

wash with 30 ml. of cold water. Precipitate as before and heat on the steam bath for 20 minutes, bringing the temperature to 45° to 50° C. [This second precipitation is necessary to free the selenium from sensible quantities of impurities.] Allow to stand 48 hours. Gather the selenium on an asbestos mat in a Gooch crucible and wash with cold water. Prepare a tare in a similar manner. Dry at 85° to 90° C. overnight, cool in a vacuum desiccator, and weigh against the tare.

*Special Treatment with Sulfuric Acid.*—If the soil contains 0.1 p.p.m. or less of selenium, use preferably the integration method. In order to accomplish this, add the distillate to a fresh charge of the soil with additional HBr and Br<sub>2</sub>. [This procedure may be repeated until any desired amount of the sample has been used.] If the soil is calcareous, lateritic, or of high colloid content, add H<sub>2</sub>SO<sub>4</sub> to the charge so that the water liberated in the reaction will not dilute the acid distillate and thereby fail to carry over the selenium. [A simple, small hydrometer may be made for use in the receiving flask and calibrated with HBr and water.] If the distillate is less than 42 percent HBr, take a second distillate and increase the amount of H<sub>2</sub>SO<sub>4</sub> correspondingly. If too much H<sub>2</sub>SO<sub>4</sub> has been added and hydrogen bromide gas passes as a fog through the Br<sub>2</sub> water trap, add water through the thistle tube to correct this. In the regular distillation of lateritic soils, add H<sub>2</sub>SO<sub>4</sub> to the charge to produce a distillate of 42 percent HBr, or stronger.

The method, essentially as described, has played a great part in selenium investigations. With slight modifications its usefulness has been greatly expanded. A few of the modifications frequently utilized by analysts include these:

1. The so-called integration concept mentioned above involves the combining of distillates from two or more individual samples (154). If distillates from as many as 10 separate samples are combined, the final determination will be based on a quantity increased tenfold from that of an individual sample. This procedure is often used for analysis of waters and other materials of very low selenium content.

2. A mixture of concentrated sulfuric and nitric acids is preferable to hydrobromic acid and bromine for preliminary digestion, when such organic materials as vegetation and animal tissues are being analyzed.

3. In certain cases titration of recovered selenium has been recommended as a final step in the determination instead of a colorimetric comparison (39). This procedure has been used success-

fully, particularly when the contents of selenium are relatively high. This involves use of a sodium thiosulfate iodine titration with starch as indicator.

Selenium determination as normally carried out leads to results dependable to about 0.01 part per million in soils, minerals, and vegetation and about 0.25 part per billion in the case of liquids and other materials where the integration principle is applied. As a rule, analytical results are reported in accordance with the limits indicated.

The method described above with its several modifications is widely used where selenium toxicity problems are being investigated. Since the recent discovery of selenium-deficient animal diets (see p. 52), it becomes desirable to determine even smaller quantities of this element than those noted above, particularly in feeds and feeding stuffs, than heretofore has been possible. Probably the most sensitive of all procedures consists of neutron activation by conventional methods, followed by measurement of the radioactivity induced in the selenium. The practical limit of sensitivity is reported to be 0.01 microgram of selenium. Leddicotte and Reynolds published a general discussion of activation analysis in 1951 (108).

In recent years another method of high sensitivity has been developed. This method is essentially a colorimetric one, depending upon a spectrophotometric measurement of a yellow derivative of selenious acid and 3,3'-diaminobenzidine as described by Cheng (35). This is said to be sensitive to 50 parts per billion with a 1-cm. cell.

Very recently a fluorometric method using 3,3'-diaminobenzidine has been developed by Watkinson (202) for determining as little as 0.02 $\mu$ g. of selenium in plants and other materials. The method appears to have promise as a means of determining small quantities of selenium. The procedure has not, however, been tried in our laboratories.

Marked progress has been made in the development of a satisfactory method for determination of extremely small quantities of selenium. However, most chemists feel that more work is necessary before a method can be recommended as sufficiently sensitive and reliable for use in studies currently underway and projected. A method of this type is needed very much because of the important shift in interest from studies of selenium as a toxic element to studies concerned with threshold values in feeds for normal animal nutrition.



# Selenium Content of Soils<sup>4</sup>

By H. W. LAKIN

The selenium in soils may be derived (1) from parent material weathered from the underlying rock; (2) from wind- or water-deposited seleniferous materials; (3) from ground or surface water, by precipitation; (4) from volcanic emanations brought down by rain; and (5) from sediments derived from mining operations. All these types are known.

Data on the selenium content of soils were summarized by Swaine in 1955 (176). This section is not intended to duplicate Swaine's work, but to point out the significance of various aspects of soil chemistry in the availability of selenium to plants.

The relations between the selenium content of soils and that of the plants grown on them are complex. For some complexities, explanations are available in the literature; for others, the causes are unknown. The nontoxic seleniferous soils, although their selenium content may be high, yield no selenium to plants; yet the toxic seleniferous soils yield enough selenium to plants to make the vegetation very toxic, in spite of the fact that the total selenium content of these soils may be appreciably lower than that of the nontoxic soils.

Studies made of toxic and nontoxic seleniferous soils have revealed that climate and soil-development processes are major factors in the availability to plants of the selenium in soils. The alkaline seleniferous soils of semiarid Western States produce toxic vegetation, whereas the acid seleniferous soils of the humid interior of Puerto Rico produce vegetation free of detectable amounts of selenium. In general, seleniferous Pedocals are toxic and Pedalfers are nontoxic.<sup>5</sup>

The selenium content of plants grown on the Pedocals of Western United States has no direct relation to either the total or the water-soluble selenium content of those soils. Plants grown in sand cultures that contain the same amount of water-soluble selenium as that contained by our western seleniferous soils absorb more than 10 times as much selenium from their growth medium as the same species of plant absorbs from the soil whose water-soluble selenium content approximates the sand culture. Other factors than the presence of selenium in the soil solution must be operative;

but adequate knowledge of these factors is still lacking.

## TOXIC SELENIFEROUS SOILS— PEDOCALS

The toxic soils of the United States are Pedocal soils; they are alkaline in reaction, they contain free calcium carbonate, and they lie in regions of low rainfall—less than 20 inches mean annual precipitation. Toxic seleniferous soils of Canada, South America, and Israel are similar. The major wheat-producing areas of the world are regions of Pedocals, and commercial wheat from various parts of the world examined by Robinson (154) contained from 0.1 to 1.9 p.p.m. selenium.

That a small pasture may yield grass ranging in selenium content from less than 1 p.p.m. to as much as 50 p.p.m. demonstrates the fact that the seleniferous soils of our Western States are not uniformly toxic. Although the erratic variation of selenium content in the surface soil yields little or no information on the toxicity, variation of selenium content with depth may provide some guide in the matter (surface in this text means from 0 to 6 or 8 inches in depth).

Byers and his coworkers (23, 24, 27) reported the selenium content of thousands of surface soils in North Dakota, South Dakota, Montana, Wyoming, Nebraska, Kansas, Colorado, New Mexico, Utah, and Arizona. The amounts of selenium in these surface soils showed no correlation with the amounts of selenium found in the vegetation sampled, other than that when selenium was present in the plants, it was present in the soils in amounts of 0.1 p.p.m. or more. Byers (23) investigated the variation of selenium content of the surface soil within a square mile area of gently rolling land in Gregory County, S. Dak. The underlying seleniferous shales were horizontal, and it was expected that the variation of the selenium in the soils might reflect vertical variations in the parent rocks. A topographic map with a 10-foot contour interval was prepared of the area and on this was plotted the selenium content of the soil (fig. 5). No relation was apparent between the selenium content and the topography—nor was there any grouping of high and low selenium concentrations. A soil containing 0.5 p.p.m. lay between soils containing 5 and 8 p.p.m.

<sup>4</sup> Publication authorized by the Director, U.S. Geological Survey.

<sup>5</sup> Pedocals and Pedalfers are defined by Marbut (117).

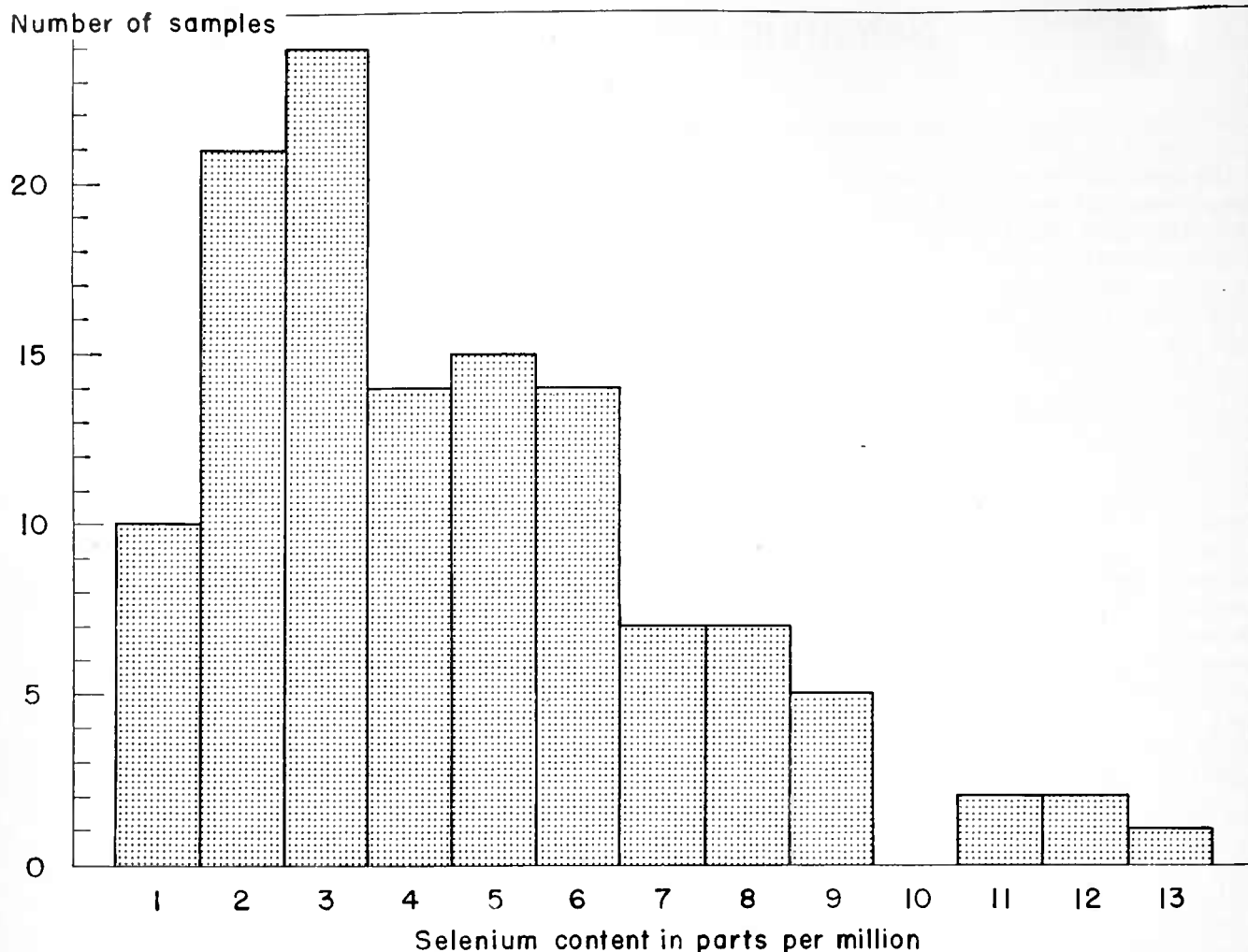


Figure 5.—Selenium content of the 122 samples of surface soils (0 to 7 inches) from sec. 21, T. 100 N., R. 72 W., Gregory County, S. Dak.

selenium. Selenium contents range from 0.5 to 13 p.p.m., the average content is 4.5, and the median 4.0; yet 45 samples contained only 2.0 to 3.5.

When the surface soil is analyzed, it does not give a true picture of the selenium content of the soil in which even shallow-rooted plants feed, because the selenium content may vary considerably within the soil profile. This variation is illustrated by a few representative profiles from Western United States (table 15). In some areas the selenium content is low near the surface and increases considerably with depth. Two trends may be seen in the data here listed: One is the increase in selenium content of soils with depth; and the second is the slight tendency for selenium to accumulate in the upper parts of some profiles—most pronounced in the profile from Fre-

mont County, Colo., but also evident in the Boyd County, Nebr., and Pueblo County, Colo., profiles.

### NONTOKIC SELENIFEROUS SOILS—PEDALFERS

No acid soils are known to produce toxic seleniferous vegetation. The nontoxic seleniferous areas are Pedalfer soils; they usually have a pH range of 4.5 to 6.5; they are characterized by a zone of accumulated iron and aluminum compounds and are developed under humid conditions. The selenium present in these soils is associated with the iron and is probably in the form of a very insoluble basic ferric selenite. If the selenium occurred as selenate, it would normally be leached out of the soil. The selenium content of



TABLE 15.—*Variation of selenium in soil profiles of Western United States*

PROFILE 1, BOYD CLAY, SEC. 1, T. 33 N., R. 10 W., BOYD COUNTY, NEBR. (BYERS, 23)

Laboratory No.	Depth	Se	Laboratory No.	Depth	Se
	<i>Inches</i>	<i>P.p.m</i>		<i>Inches</i>	<i>P.p.m.</i>
B-843.....	0-6	3.0	B-829.....	36-42	3.0
B-844.....	6-12	3.0	B-830.....	42-48	3.0
B-845.....	12-18	2.0	B-840.....	48-54	12.0
B-846.....	18-24	2.0	B-841.....	54-60	28.0
B-827.....	24-30	2.0	B-842.....	61-72	24.0
B-828.....	30-36	2.0			

PROFILE 8, BOYD CLAY LOAM, SEC. 35, T. 2 N., R. 30 E., JONES COUNTY, S. DAK. (BYERS, 23)

B-12089.....	0-12	2.5	B-12092.....	36-48	3.0
B-12090.....	12-24	4.0	B-12093.....	48-60	3.5
B-12091.....	24-36	4.0	B-12094.....	60+	3.5

VALE FINE SANDY LOAM, SEC. 30, T. 8 N., R. 7 E., BUTTE COUNTY, S. DAK. (BYERS, 23)

B-11786.....	0-10	0.2	B-11789.....	35-46	0.4
B-11787.....	10-24	.2	B-11790.....	46-60	.5
B-11788.....	24-35	.3			

PROFILE 17, NIOBRARA SILT LOAM, PUEBLO COUNTY, S. DAK. (BYERS AND OTHERS, 27)

B-19616.....	0-6	5.0	B-19620.....	36-48	3.0
B-19617.....	6-12	5.0	B-19621.....	48-58	3.0
B-19618.....	12-24	4.0	B-19622.....	58-62	12.0
B-19619.....	24-36	5.0			

PROFILE 18, NIOBRARA SILT LOAM, SEC. 9, T. 18 S., R. 70 W., FREMONT COUNTY, COLO. (BYERS AND OTHERS, 27)

B-19644.....	0-1	38.0	B-19648.....	10-14	42.0
B-19645.....	1-4	26.0	B-19649.....	14-26	54.0
B-19646.....	4-6	22.0	B-19650.....	26-32	98.0
B-19647.....	6-10	24.0	B-19651.....	36-40	48.0

Pedalfers has not been studied extensively. Only two areas of seleniferous Pedalfers are known—one in Hawaii and the other in Puerto Rico.

The selenium content of samples from six soil profiles from the Hawaiian Islands—three from the island of Maui, and three from the island of Kauai—are given in table 16. In these, the selenium content decreases with depth and with decreased rainfall. Byers and others (27) postulated that the selenium in these soils is brought down by rain from volcanic emanations and dust and is fixed as a basic ferric selenite. Certainly soils containing as much as 26 p.p.m. of selenium under an annual rainfall of 100 inches do not contain selenium in a very soluble form. The pH of these soils is between 4.5 and 5.5 (Hough and Byers, 84). Although the soils contain as much as 26 p.p.m., 3 p.p.p. is the highest reported sele-

nium content of plants grown in them (Byers and others, 27).

Another illustration of the unavailability of selenium to plants in acid soils is provided by the soils developed from the seleniferous Fajardo shale (Roberts and party, 152) in the mountainous interior of Puerto Rico (table 17). One of these soils, the Yunes clay, was developed on a steep slope under an annual precipitation of 80 inches; another, the Yunes silt loam, was developed under an annual rainfall of 55 inches. Selenium content of soils from this area ranges from 1.0 to 12.0 p.p.m., and of the underlying Fajardo shale from 2.5 to 8.0 p.p.m. (Williams and others, 208). J. I. Otero collected and classified every type of vegetation growing in the Yunes silt loam on a 40-acre tract (Lakin and others, 103). None of these plants contained as much as 1 p.p.m. of selenium.

TABLE 16.—*Variation of selenium content in soil profiles, Hawaiian Islands*<sup>1</sup>

Island and laboratory No.	Location	Rainfall	Material		Se
			Texture	Depth	
Island of Maui:		<i>Inches</i>		<i>Inches</i>	<i>P.p.m.</i>
B-5787	156°39'40'' W., 20°56'20'' N.; elevation, 2,500 feet.	100	{ Red clay	0-6	7
B-5788			{ Red clay	6-9	15
B-5789			{ Red clay	9-30	18
B-5790			{ Lava and soil	30-40	8
C-938	5 mi. N. by NE. of Lahaina; elevation, 2,550 feet.	100	{ Silty clay loam	0-7	8
C-939			{ Silty clay loam	7-15	26
C-940			{ Silty clay loam	15-22	3
C-941			{ Silty clay loam	22-30	2
B-5791	156°40'24'' W., 20°58'24'' N.; elevation, 450 feet.	20	{ Clay loam	0-2	1
B-5792			{ Clay loam	2-7	3
B-5793			{ Clay loam	7-28	.6
B-5794			{ Clay loam	28-50	1
Island of Kauai:					
B-3717	159°27'48'' W., 22°12'36'' N.; elevation, 500 feet.	100	{ Red clay	0-4	15
B-3718			{ Red clay	4-16	15
B-3719			{ Red clay	16-33	12
B-3720			{ Red clay	33-50	12
B-3721			{ Red clay	2 20	.4
C-784	2 mi. south of Kalihiwai	90	{ Kalihiikai silty clay	0-6	10
C-785			{ Kalihiikai silty clay	12-20	6
C-786			{ Kalihiikai silty clay	20-54	2
C-792	0.75 mi. north of Hanapepe	25-30	{ Hanapepe	0-8	1
C-793			{ Hanapepe	8-14	1
C-794			{ Hanapepe	14-32	1
C-795			{ Hanapepe	35-42+	1

<sup>1</sup> Data from Byers and others (27).<sup>2</sup> In feet.TABLE 17.—*pH and selenium content of nontoxic Puerto Rican soil profiles*<sup>1</sup>

Soil type	Soil Survey No.	Depth	pH	Se
		<i>Inches</i>		<i>P.p.m.</i>
Yunes clay	5802141	0-6	4.6	1.0
Do	5802142	6-9	4.1	1.5
Do	5802143	9-30	3.9	1.5
Yunes silt loam	5803115	0-4	5.1	1.5
Do	5803116	4-14	4.3	2.0
Do	5803117	14-28	4.2	10.0

<sup>1</sup> Data from Roberts and party (152, tables 36 and 56).

## PROPERTIES OF TOXIC SELENIFEROUS SOILS

Although many factors govern the selenium uptake by plants, a partial measure of selenium's availability to plants is its solubility in water. Toxic soils contain water-soluble selenium; the others do not. From the physical chemistry of selenium one finds that it may be oxidized to selenates in a moist alkaline environment; the formation of selenates in an acid environment is not

likely. One may conclude that in regions of low rainfall, the alkaline seleniferous soils will contain  $\text{CaSeO}_4$ , which is soluble in water and available to plants; in regions of high rainfall, the acid seleniferous soils will not contain selenic acid, which, if formed, would be leached out of the soil. The seleniferous soils of Ireland lie between these two extremes and are an interesting example of the mobility of selenium in a humid climate. In addition to water-soluble selenates, water-soluble organic selenium has been found in our Western States.

Sulfates decrease the uptake of selenates by plants, and sulfates are usually present in the seleniferous soils; however, the addition of more sulfur to these soils has no discernible effect. Soil colloids have practically no effect on the availability of selenates to plants, although these diminish the availability of selenites.

The relatively low annual rainfall in seleniferous areas of the United States minimizes the leaching of selenates from the soil. A Pierre clay profile—pH 8.1 to 8.5—from Gregory County, S. Dak., where the mean annual rainfall is 14.54 inches, was examined by Brown and Byers (22) (table 18). They found calcium sulfate accumulating in the 60- to 74-inch horizon and com-

TABLE 18.—*Soluble salts, pH, and selenium content of a toxic soil profile (Pierre clay), Gregory County, S. Dak.*<sup>1</sup>

Sample No.	Depth	pH	Soluble salts	Se
	<i>Inches</i>		<i>P.p.m.</i>	<i>P.p.m.</i>
B-858-----	0-8	8.3	860	5.0
B-895-----	8-18	8.5	760	6.0
B-894-----	18-40	8.4	780	4.0
B-857-----	40-60	8.1	1,260	5.0
B-893-----	60-74	8.2	9,800	6.0

<sup>1</sup> Data from Brown and Byers (22, table 14).

mented: "In the general run of the Pierre soils the zone of sulfate accumulation is nearer the surface than in the present profile. It may be remarked that while the zone of carbonate accumulation may be regarded as marking the maximum mean penetration of water, the zone of sulfate accumulation marks the maximum depth of penetration of moisture." Certainly the 9,800 p.p.m. of soluble salts that these authors found in the 60- to 74-inch horizon suggests that little leaching is taking place beyond this depth. In this environment selenium could be oxidized to selenate and the soluble selenates could remain in the soil.

To ascertain how much selenium is soluble in seleniferous soils, Williams and Byers (207) determined the selenium in water extracts of a hundred samples of seleniferous soils, and found that the soils contained from less than 0.1 to 38 p.p.m. water-soluble selenium. They concluded that probably most of the soluble selenium was in the form of calcium selenate.

Olson and others (138) studied the occurrence of soluble selenium in soil profiles from sec. 2, T. 107 N., R. 78 W., South Dakota (table 19). These authors stated that the water-soluble selenium is almost entirely selenate, because it was not appreciably reduced by SO<sub>2</sub> in 6 N sulfuric acid. They concluded that the weathering processes in this region oxidize a large part of the selenium to the selenate form, which may then be leached from the near-surface soil and moved to the subsoil or removed by runoff waters and redeposited at lower elevations. These workers observed a relationship between the apparent leaching of selenium in the soils and the selenium content of the plants and stated: "With few exceptions, where plants of the higher selenium contents are found the amount of the element in the soil increases with depth." Hurd-Karrer (88) found tenfold as much selenium (350 p.p.m.) in wheat grown in a sand culture containing 2 p.p.m. selenium as is reported for *A. smithii* (35 p.p.m.) in table 19, soil No. 14. These data and other data in the literature strongly suggest that solubility of selenium is not the only factor involved.

TABLE 19.—*Relation of soluble selenium in soils to selenium in vegetation*<sup>1</sup>

Soil No. and depth <sup>2</sup>	Total Se content of soils	Soluble Se content of soils	Se content of <i>Agropyron smithii</i> <sup>3</sup>
	<i>P.p.m.</i>	<i>P.p.m.</i>	<i>P.p.m.</i>
6: 1st foot-----	2.7	0.12	18
2d foot-----	5.5	2.76	-----
3d foot-----	11.5	.58	-----
7: 1st foot-----	4.3	.43	79
2d foot-----	15.8	5.00	-----
3d foot-----	29.0	10.85	-----
8: 1st foot-----	3.0	1.43	8
2d foot-----	4.5	.48	-----
3d foot-----	11.5	2.66	-----
14: 1st foot-----	4.4	0.91	35
2d foot-----	28.4	17.60	-----
3d foot-----	38.4	18.99	-----
21: 1st foot-----	4.4	.08	2
2d foot-----	4.8	.10	-----
3d foot-----	6.4	.12	-----
32: 1st foot-----	5.9	.11	2
2d foot-----	4.6	.05	-----
3d foot-----	6.0	.11	-----

<sup>1</sup> Data from Olson and others (138).

<sup>2</sup> Soil location was an area in sec. 2, T. 107 N., R. 78 W., South Dakota.

<sup>3</sup> Results of analyses of composited samples taken over a 5-yard radius from the sampling point of each soil sample.

As annual rainfall increases, the movement of selenium in ground waters becomes more evident (195). In western South Dakota, northwestern Nebraska, and eastern Colorado, selenium enrichment in the subsoil sometimes results from leaching of the topsoil. In northeastern South Dakota and north-central North Dakota, evidence of removal from the soil is found. Depressions in soils developed on Pleistocene deposits in northeastern South Dakota, as reported by Searight and Moxon (164), and soils formed from Pleistocene lacustrine deposits in North Dakota, as reported by Lakin and Byers (102), contained more selenium than did the adjacent glacial drift. Lakin and Byers suggested that selenium leached from the surrounding drift had enriched the low-lying lacustrine materials. The most impressive example of selenium enrichment of low-lying lacustrine soils by ground waters is found in the most highly seleniferous soils reported in the literature—those of Limerick, Tipperary, and Meath Counties, Ireland (Walsh and Fleming, 200, 201; O'Moore, 139; and Fleming and Walsh, 55). Fleming and Walsh reported soils containing as much as 1,200 p.p.m. selenium, a figure tenfold that of the selenium content of the most seleniferous soils reported in the United States.

Fleming and Walsh (55) observed that the highest selenium concentrations found in the Irish soils are associated with the organic-rich horizons. Data selected from the work of these authors are given in tables 20 and 21. In all three areas ex-

TABLE 20.—*Selenium content of toxic and nontoxic soil profiles in relation to pH and organic matter, County Tipperary, Ireland*<sup>1</sup>

Toxic profile				Nontoxic profile			
Depth (inches)	pH	Se	Organic matter	Depth (inches)	pH	Se	Organic matter
		<i>P.p.m.</i>	<i>Percent</i>			<i>P.p.m.</i>	<i>Percent</i>
0-6-----	7.2	19.6	31.0	0-6-----	5.4	1.27	9.5
6-12-----	6.5	175.0	75.0	6-12-----	5.7	1.46	3.5
12-20-----	7.7	6.9	6.6	12-18-----	5.9	.74	1.1
20-24-----	7.1	100.1	62.6	>18-----	8.1	.56	0.7
24-34-----	7.3	2.1	3.0	-----	-----	-----	-----
>37-----	7.9	.6	1.1	-----	-----	-----	-----

<sup>1</sup> Data from Fleming and Walsh (55, table 5).

amined by Fleming and Walsh the highest selenium contents were found in low-lying, poorly drained, highly organic soils; the adjacent well-drained Brown Earth soils were relatively low in selenium, were acid in reaction, and did not produce toxic vegetation. The data in table 20 show a marked correlation between selenium and organic matter in the toxic profile. The highly organic horizons are also the least alkaline; and, as might be expected, the data in table 21 show that water-soluble selenium constitutes a smaller percentage of the total selenium in organic horizons than is found in presumably more alkaline horizons of lower selenium and organic content. These extremely seleniferous areas in Ireland apparently have resulted from transportation of water-soluble selenium into a poorly drained organic reducing basin. The selenium in the area has been redistributed by ground water as a result of alternate oxidation and reduction. Although these soils are very high in total selenium, they are low in water-soluble selenium as compared to the soils of South Dakota (table 19) and of Israel (table 22). The Irish soils are unique in being the only known seleniferous soils producing toxic vegetation in a humid climate. The toxic vegeta-

tion, however, is confined to soils of alkaline reaction.

Water-soluble selenium makes up as much as 30 percent of the total selenium in some toxic soils of Israel (table 22) studied by Ravikovitch and Margolin (150). These are calcareous alluvial soils with a pH 7.8 to 8.2. Although the maximum selenium content found in the soils in the Huleh Valley is 6 p.p.m., alfalfa grown there contained from 1.4 to 44 p.p.m. selenium. Alfalfa that grew on soils containing only 0.1 to 0.3 p.p.m. of total selenium accumulated up to 14 p.p.m. A native deep-rooted plant, *Prosopis farcta* (Russ.) Macbr., growing in the Huleh Valley, contained 136 to 311 p.p.m. of selenium. The selenium content of plants growing on these soils serves to demonstrate that high total selenium in soils is not the determining factor for toxicity of vegetation in seleniferous lands. In contrast, the highest selenium content in vegetation from the highly seleniferous Hawaiian soils reported by Byers and others (27) is 3 p.p.m.

Not all water-soluble selenium in soils occurs as selenates. In soil containing 40 p.p.m. selenium, Williams and Byers (207) found about 10 p.p.m. of water-soluble selenium that was neither selenate nor selenite selenium. They postulated that this fraction was composed of organic selenium compounds, since the selenium in green vegetation is largely water-soluble. Beath and others (16) reported on a sample of the top 20 inches of soil in northeastern Niobrara County, Wyo., that contained 22 p.p.m. total selenium, 2.6 as selenate, and 6.0 as soluble organic selenium. A sample of the soil from a depth of 20 to 40 inches contained 32 p.p.m. total selenium, 9.5 as selenate, and 3.4 as soluble organic selenium. The highest selenium content reported for any vegetation is 14,920 p.p.m. in *Astragalus racemosus* Pursh found by Beath on this soil (Beath and others, 16). A water leachate of such seleniferous plant material would indeed be rich in selenium.

Beath and his associates (11) have attached much significance to the part played by "con-

TABLE 21.—*Total and water soluble selenium in toxic soil profiles from County Limerick, Ireland*<sup>1</sup>

Profile No.	Depth	Total Se	Water soluble Se	
			P.p.m.	Percentage of total
	<i>Inches</i>	<i>P.p.m.</i>		
3-----	0-6	63.4	1.48	2.34
	6-12	207.0	1.29	.62
	24-36	225.0	1.41	.63
4-----	0-6	53.5	.25	.46
	12-24	850.0	2.81	.33

<sup>1</sup> Data from Fleming and Walsh (55, table 7).

TABLE 22.—*Total and water soluble selenium in toxic Israeli soils*<sup>1</sup>

Location	Soil No.	Depth	Total Se	Water soluble Se	
				P.p.m.	Percentage of total
Naot-Mordechai (Huleh Valley)-----	6	<i>Feet</i> 1	<i>P.p.m.</i> 4.0	0.3	7.5
Do-----		2	2.0	.4	20.0
Do-----	12	1	6.0	.5	8.3
Do-----		3	2.0	.6	30.0
Do-----	68	1	3.8	.3	7.9
Nir David (Beit Shan Valley)-----	57	2	.4	.05	12.5

<sup>1</sup> Ravikovitch and Margolin (149, table 3).

verter" plants in making selenium available to other types of vegetation. However, Olson, Whitehead, and Moxon (138), in their study of South Dakota soils, state: "The importance of converter plants in the soils studied here is not known, but it appears quite probable that weathering has played the dominant role in the freeing of selenium from its insoluble forms." Although soluble organic selenium compounds no doubt play a part in supplying selenium to crops, Beath and others (16) concluded that in the toxic areas investigated by them selenate selenium is the dominant water-soluble form and that this form is more toxic to nonaccumulator plants than is the organic form.

## REDUCTION OF TOXICITY BY SOIL AMENDMENTS

A means to inhibit the absorption of selenium by plants has been sought to permit safe utilization of seleniferous soils for agricultural purposes. In a study of Belle Fourche irrigation project, Butte County, S. Dak., Byers (23) observed that if the sulfur-selenium ratio is 50 or more, the selenium content of the vegetation is low. Hurd-Karrer and Kennedy (90) showed that the addition of sulfur or gypsum to the Keyport clay, made seleniferous by the addition of 2 p.p.m. selenium as sodium selenate, reduced the uptake of selenium by young winter wheat to one-tenth the amount absorbed in the absence of sulfur or gypsum. Further experiments with wheat grown in nutrient solutions (Hurd-Karrer, 89) showed that sulfur inhibited the uptake of selenate selenium but not of selenite selenium. Numerous greenhouse experiments have confirmed these observations (Hurd-Karrer, 88, Gile and Lakin, 69, Trelease and Beath, 185).

The effects of soluble sulfates upon the selenium uptake of plants in natural surroundings are difficult to evaluate. Franke and Painter (61) tested the effect of adding sulfur to plots in a 12-acre field in Gregory County, S. Dak., where surface soil contained an average of 446 p.p.m. of

sulfur before any additions were made. Enough sulfur was added, both as native sulfur and as gypsum, to triple the sulfur content of the upper 6 inches of soil. No decrease in the selenium content of corn or wheat grain was noted following the treatment. The total selenium content of the surface soil (0-6 inches) ranged from 2.0 to 3.7 p.p.m. No data are presented on the water-soluble selenium nor on the selenium content of lower horizons. The authors concluded that sulfur applications failed to inhibit the absorption of selenium by plants. Brown and Byers (22) give data on the soluble salts (presumed by these authors to be sulfates) and selenium content of a Pierre clay from Gregory County, S. Dak. The soluble salts in this profile range from 760 to 9,800 p.p.m., and selenium from 4 to 6 p.p.m. (table 18). The sulfur-selenium ratio in this profile ranges upward from about 30. Most of the controlled experiments have been at lower ratios. Beath (5) concludes that the "sulfur-selenium antagonism theory has not been found generally applicable to farm and range practices of the Rocky Mountain region."

In greenhouse experiments, Ravikovitch and Margolin (149) supplied monocalcium phosphate, calcium sulfate, and barium chloride to Israeli soils containing 4.0 and 0.5 p.p.m. selenium, in order to determine their inhibitory effect. The monocalcium phosphate had little effect, which confirms the results of Gile and others (68) on the growth of millet in soils made seleniferous with sodium selenate. Considerable quantities of gypsum caused a significant reduction in the selenium uptake by alfalfa. The effectiveness of barium chloride in small quantities was exceptionally pronounced; it stopped completely the absorption of selenium by alfalfa from the soil of lower selenium content.

The generally high sulfur-selenium ratios prevalent in our western soils preclude the possibility of determining what the selenium content of vegetation might be in the absence of abundant sulfates. The seleniferous Irish soils, however, may give some insight into the beneficial effects of the

presence of plentiful sulfates in our seleniferous soils. As noted earlier, the Irish soils are high in total selenium but low in water-soluble selenium; the maximum water-soluble selenium (Fleming and Walsh, 55) is 2.81 p.p.m. In South Dakota soils, Olson and others (137) reported 19 p.p.m. of water-soluble selenium; and Williams and Byers (207) found 38 p.p.m. However, a survey of wheat grain from Western United States (Williams and others, 209) showed a maximum of 25 p.p.m., as contrasted to 164 p.p.m. in wheat grain from the Irish soils reported by Fleming and Walsh (55). The fact that grasses absorb selenium only in small quantities in the Western

States is commented on as follows by Fleming and Walsh: "Our experience does not agree with this as can be seen from the relatively high levels present in some of the herbage species from our pot experiments, while in addition \* \* \* levels up to 500 p.p.m. have been obtained on mixed herbage samples." Because of the high rainfall one would not expect to find an appreciable amount of sulfates in the Irish soils and nothing in the literature indicates high sulfate content. It is probable that the abundant sulfates in the seleniferous soils of the United States have greatly diminished the selenium uptake by cultivated crops.

## Occurrence and Significance of Selenium in Plants

By K. C. BEESON

The detection of selenium in plants was announced in 1932 by the French chemist Taboury (177), and the first quantitative determination of this element in plants was reported by Robinson in 1933 (153). As early as 1880, however, Cameron (29), after the addition of selenium to a soil, noted a chlorosis in the plants growing thereon. He postulated that selenium was absorbed by the plant and might be substituting for sulfur in some of the sulfur compounds in the plant. The literature now contains reports of thousands of analyses of a wide variety of both native and crop plants, indicating that selenium must indeed be readily absorbed by all members of the plant kingdom. Of special interest in this respect is the occurrence of selenium in food plants with the possible detrimental effects on public health. With this aspect of the problem in mind a number of reports have appeared on the selenium content of wheat grown in many parts of the world (10, 94, 100, 123, 143, 154, 183, 208).

Robinson (153) and Lakin and Byers (100), from their extensive work on this crop, suggest that selenium is present in all wheat in detectable amounts. There appears to be no basis for concern, however, for very few samples analyzed have contained toxic quantities and the dilution of these crops with nonseleniferous wheat minimizes any danger. Of the samples reported by Robinson (153), two contained levels of selenium toxic to rats—5 and 11 p.p.m. Lakin and Byers (100) reported that 82.5 percent of 951 samples of wheat examined by them contained 1.0 p.p.m. or less of selenium, 10 percent contained 2 to 3 p.p.m., 7.5 percent contained 4 p.p.m. or more selenium, and of these only 8 samples contained as much as 10 p.p.m. or more. Thorvaldson and Johnson (183) reported a mean value of 0.44 p.p.m. of selenium in 2,230 samples of wheat from Canada. The maximum was 4.0 p.p.m. Robinson (153) found 26 p.p.m. of selenium in one sample of toxic

wheat, but reported 0.1 to 1.5 p.p.m. in 29 samples from various parts of the world. Although a human tolerance for selenium is not known, it appears doubtful that any substantial quantity of selenium occurs in our food supply from this crop.

Williams, Lakin, and Byers (209) have published analyses of a number of crops grown in the seleniferous soils of Western United States. In general the levels in the majority of samples collected range from 0.1 to 4 p.p.m. Very few values as high as 15 p.p.m. are reported. One sample of rye, 25 p.p.m., and one of corn, 30 p.p.m., were notable exceptions. There appears to be little evidence that alfalfa will absorb large quantities of selenium. Both Moxon (123), at the South Dakota Agricultural Experiment Station, and Beath, Eppson, and Gilbert (12), at the Wyoming Station, have conducted surveys of this kind. Beath and coworkers harvested a crop of alfalfa from a field formerly containing two "indicator" or "converter" plants, *Astragalus pectinatus* Dougl. and *A. bisulcatus* (Hook.) Gray. Selenium was not detected in the alfalfa, and when it was fed to rabbits no toxicities were observed. While, in general, conclusions that alfalfa is not ordinarily seleniferous are probably valid, a few high values in alfalfa have been reported by Byers (24).

## SPECIES DIFFERENCES IN THE ABSORPTION AND ACCUMULATION OF SELENIUM

The first indication of a species difference in the absorption of selenium was that made by Taboury (177), who detected selenium in only two of three plants collected from one locality. Beath and coworkers (8) had observed early in their studies that not all plant species growing on certain shales and other geological formations were toxic to animals. However, evidence that



significant quantitative differences do occur among species growing in the same soil was first presented by Hurd-Karrer (86), who studied the problem under uniform conditions in the greenhouse. Her data show that the greatest accumulation of selenium occurred in the two representatives of the Cruciferae—mustard and broccoli. This family also accumulates large quantities of sulfur. All plants studied under these conditions absorbed more selenium than is normally absorbed by similar plants in seleniferous areas.

As field surveys became more extensive, many workers observed this difference in the ability of plants to absorb selenium. Beath, Eppson, and Gilbert (11) noted that different species of *Astragalus* were not at all uniform in this respect, even when grown in close proximity to one another. Miller and Byers (119) collected a number of plants from a small seleniferous area in Colorado. Unfortunately, at least four soil types appear to be represented, but the data indicate that wide differences may be expected in the selenium content of different plant species. *Astragalus pectinatus* contained about 4,000 p.p.m. of selenium, whereas blue gramagrass contained only 2 p.p.m. *Stanleya pinnata* (Pursh) Britt. and *Haplopappus fremontii* Gray were also absorbers of excessive quantities of selenium. Other studies by Byers (23) and Williams, Lakin, and Byers (209) show that the grasses are relatively poor selenium accumulators as compared to many other plants. Thus, in a soil where the selenium concentration in buckbrush was 12 p.p.m., little bluestem contained only 1 p.p.m. Also, in another soil, wild aster contained 120 p.p.m. and associated grasses contained only 6 p.p.m. of selenium (23). Fourteen plant species collected from another area 100 feet square showed a range in selenium concentration of 0.5 to 20 p.p.m. The lowest values were found in the grasses.

Hence, Byers, Miller, Williams, and Lakin (27) decided that plants may be grouped with reference to their relation to selenium absorption. Those absorbing little selenium included the grasses—buffalograss and gramagrass, in particular. Those able to absorb moderate amounts of selenium included the common cereals and a number of such native plants as wreath aster, blue aster, turpentineweed, and the sunflower. The third group included plants that absorb selenium readily. These include *Astragalus racemosus*, *A. pectinatus*, *A. bisulcatus*, *A. carolinianus* L., *A. grayii* Parry, *Stanleya pinnata*, *S. pinnata* var. *bipinnata* (Greene) Rollins, *Haplopappus fremontii*, and *Xylorrhiza parryi* (Gray) Greene. Moxon, Olson, and Searight (129) sampled several species within an area of about 4 square rods on the same geological formation. Their data show clearly the magnitude of the differences that may be expected in absorption of selenium by different species. Thus, *Artemisia canadensis* Michx. contained 6.8 p.p.m. of selenium as com-

pared to 2,380 p.p.m. in *Stanleya pinnata* var. *bipinnata*. In another area the contents ranged from zero in western wheatgrass to 500 p.p.m. in *Astragalus racemosus* (figs. 6 and 7).

## SELENIUM INDICATOR PLANTS

The most useful tools for study of the selenium problem have been the development by Robinson (153) of chemical methods of analysis for minute quantities of the element and the concept of indicator plants first advanced by Beath and co-workers in 1934 (8). These workers noted that certain species invariably showed the presence of selenium and occurred only on certain seleniferous geological formations. After extensive field observations on the occurrence of these and other plants (5, 6, 11, 119), Beath and coworkers published a series of reports (8, 9, 10, 11), outlining their concepts much more fully. The following list is their selection of the seleniferous *Astragalus* and other indicator plants:

Genus	Group	Species
<i>Astragalus</i> ---	<i>Bisulcati</i> -----	<i>Astragalus bisulcatus</i> (Hook.) Gray
Do-----	---do-----	<i>A. haydenianus</i> Gray
Do-----	---do-----	<i>A. oocalycis</i> M. E. Jones
Do-----	---do-----	<i>A. scobinatulus</i> Sheld.
Do-----	---do-----	<i>A. urceolatus</i> Greene
Do-----	<i>Galegiformes</i> ---	<i>A. racemosus</i> Pursh
Do-----	<i>Inflati</i> -----	<i>A. artemisiarum</i> M. E. Jones
Do-----	<i>Lonchocarpi</i> ---	<i>A. osterhoutii</i> M. E. Jones
Do-----	<i>Ocreati</i> -----	<i>A. albulus</i> Woot. Standl.
Do-----	---do-----	<i>A. argillosus</i> M. E. Jones
Do-----	---do-----	<i>A. confertiflorus</i> Gray
Do-----	---do-----	<i>A. flaviflorus</i> (O. Ktze.) Sheld.
Do-----	---do-----	<i>A. flavus</i> Nutt.
Do-----	---do-----	<i>A. moencoppensis</i> M. E. Jones
Do-----	---do-----	<i>A. sophoroides</i> M. E. Jones
Do-----	<i>Podo-sclerocarpi</i> ---	<i>A. grayii</i> Parry
Do-----	---do-----	<i>A. pectinatus</i> Dougl.
Do-----	---do-----	<i>A. pectinatus</i> var. <i>platyphyllus</i> M. E. Jones
Do-----	---do-----	<i>A. rafaensis</i> M. E. Jones
Do-----	---do-----	<i>A. loanus</i> M. E. Jones
Do-----	<i>Preussii</i> -----	<i>A. asclepiadoides</i> M. E. Jones
Do-----	---do-----	<i>A. beathii</i> Porter
Do-----	---do-----	<i>A. eastwoodae</i> M. E. Jones
Do-----	---do-----	<i>A. ellisiae</i> (Rydb.) Porter
Do-----	---do-----	<i>A. limatus</i> Sheld.
Do-----	---do-----	<i>A. pottersonii</i> Gray
Do-----	---do-----	<i>A. praelongus</i> Sheld.
Do-----	---do-----	<i>A. preussii</i> Gray
Do-----	---do-----	<i>A. preussii</i> var. <i>latus</i> M. E. Jones
Do-----	---do-----	<i>A. sabulosus</i> M. E. Jones

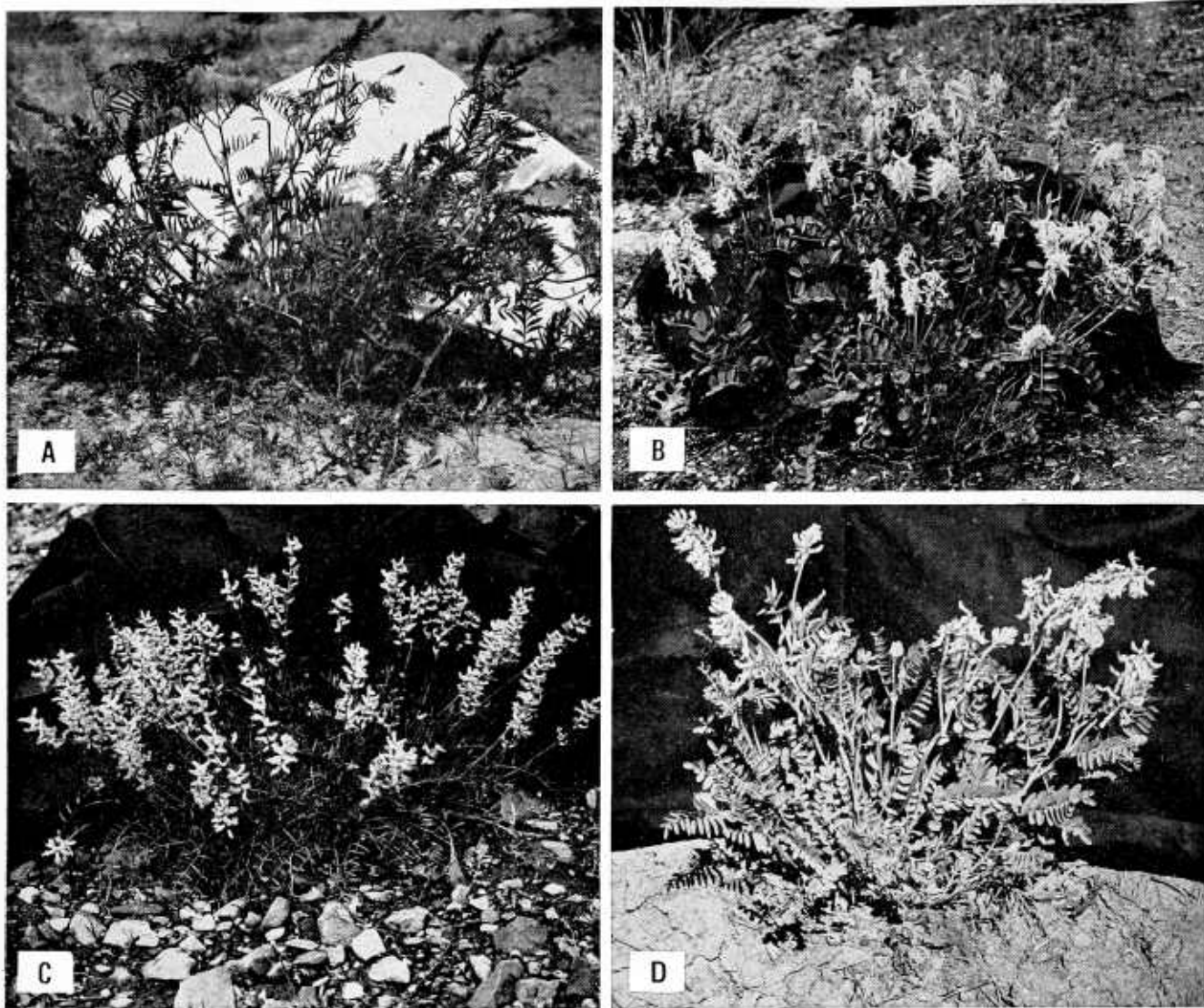


Figure 6.—Legume plants of the genus *Astragalus* are among the highest absorbers of selenium: A, *A. bisulcatus*; B, *A. canadensis* L.; C, *A. pectinatus*; and D, *A. racemosus*. (Courtesy U.S. Geological Survey.)

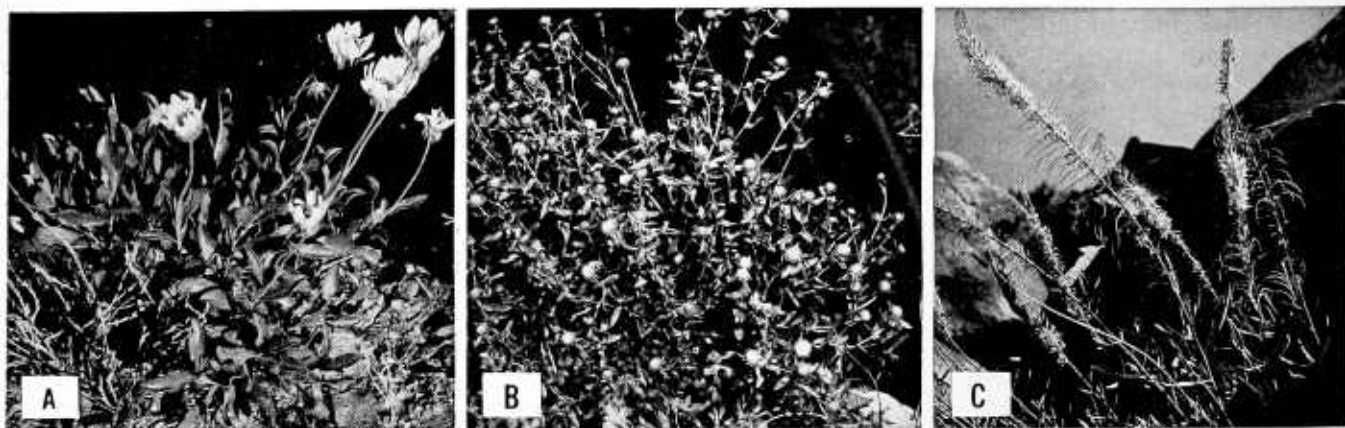


Figure 7.—Plants of different botanical groups are sometimes strong absorbers of selenium: A, *Xylorrhiza venusta* (M. E. Jones) Heller (woody aster); B, *Grindelia squarrosa* (curlycup gumweed); and C, *Stanleya pinnata* (desert princesplume).



Genus	Group	Species
<i>Stanleya</i> -----	-----	<i>Stanleya albenscens</i> M. E. Jones
Do-----	-----	<i>S. elata</i> M. E. Jones
Do-----	-----	<i>S. pinnata</i>
Do-----	-----	<i>S. pinnata</i> (Pursh) Britt. var. <i>gibberosa</i> Rollins
Do-----	-----	<i>S. pinnata</i> var. <i>bipinnata</i>
Do-----	-----	<i>S. pinnata</i> var. <i>integrifolia</i> (James) Rollins
Do-----	-----	<i>S. tomentosa</i> Parry
Do-----	-----	<i>S. viridiflora</i> Nutt.
<i>Xylorrhiza</i> -----	-----	<i>Xylorrhiza</i> <i>glabrinscula</i> Nutt.
Do-----	-----	<i>X. parryi</i>
Do-----	-----	<i>X. venusta</i>
Do-----	-----	<i>X. villosa</i> Nutt.
<i>Oonopsis</i> -----	-----	<i>Happlopappus</i> <i>fremontii</i> var. <i>wardii</i> Gray
Do-----	-----	<i>Oonopsis argillacea</i> A. Nels.
Do-----	-----	<i>O. condensata</i> A. Nels.
Do-----	-----	<i>O. engelmannii</i> (Gray) Greene
Do-----	-----	<i>O. foliosa</i> (Gray) Greene

The fact that not all species of *Astragalus* are selenium absorbers has led several workers to use this property as a basis for group reclassification of the *Astragali*. Beath (6) found that *Astragalus lonchocarpus* Torr. did not absorb selenium in toxic amounts and was not confined to seleniferous soils. *A. osterhoutii* is associated only with seleniferous soils. Lakin and Hermann (104) found that *A. artemisiarum* M. E. Jones, classified in the *Inflat* group, contained large quantities of selenium and was found only on seleniferous soils. They note that this species has several morphological characteristics in common with the seleniferous *Preussii* group and they suggest its inclusion in that group. Trelease and Trelease (190), pursuing this problem further, studied the effect of selenium in a nutrient solution on *Astragalus racemosus*, an indicator plant, and *A. crassicaarpus* Nutt., a nonindicator. The growth of *A. racemosus* was greatly stimulated by selenium, whereas *A. crassicaarpus* was retarded. They concluded that these experiments indicated a physiological basis for the differences noted in the field. Perhaps this means an actual need of relatively large quantities of selenium by certain species of *Astragalus*.

Other criteria based on selenium have been devised to improve the classification of *Astragalus*. Trelease (184) has suggested a germination test as an aid to classifying the 218 species in North America and the 1,200 species in the rest of the world. He found that the addition of 20 p.p.m. of selenium (as sodium selenite) to the culture solution has no observable effect upon the early seedling growth of an indicator species of *Astragalus*, whereas it completely inhibits root development of a nonindicator species. Vilkomerson

(196) has correlated chromosome numbers of 26 species of *Astragalus* with selenium absorption data. Eleven species, all selenium absorbers, had 24 chromosomes. Thirteen had 22 chromosomes, and of these, nine are nonabsorbers. It appeared that the *Lonchocarpi* and *Podo-sclerocarpi* groups should be subjected to further study, since these groups include species of like chromosome number and unlike reaction to selenium.

Byers and Lakin (26) suggest, on the basis of of selenium content, that *Homalobus tenellus* (Pursh) Britt. (*A. tenellus* Pursh) and *Chamaerhodos nuttalli* are selenium indicators. However, more extensive experience with these species will be necessary before this observation can be fully accepted. Moxon and others (126) have suggested *Mentzelia decapetala* (Pursh) Urb. & Gilg. as a possible indicator plant.

A somewhat different concept of an indicator plant has been utilized by Olson, Jornlin, and Moxon (137), who employed *Agropyron smithii* in an intensive study of a small area in South Dakota. This grass, common to the area, absorbs more selenium than do other grasses and appears to be a better indicator of available selenium in the soil than other species. It is not, however, restricted to seleniferous soils.

## SELENIUM CONVERTER PLANTS

In 1934 Beath, Draize, and Gilbert (9) observed that crop and forage plants growing on seleniferous shales most frequently absorb toxic quantities of selenium in those cases where indicator plants are or have been growing. To study this further, a composite sample of raw Steele shale was placed in two large pits (5, 12). Seeds of *Astragalus racemosus*, *A. grayi*, *A. bisulcatus*, *A. pectinatus*, and *Oonopsis condensata* were sown in one pit. The resulting plants were permitted to grow normally and eventually they died, decomposed, and were leached. After 3 years the surface soil in this pit produced a toxic wheat, whereas wheat grown in the control was not toxic. Hence, the authors refer to most of the indicator plants as also being "converter" plants in that they are able to absorb selenium from relatively insoluble compounds and convert it to forms readily available to other plants, including crop plants such as corn and wheat.

## DISTRIBUTION OF SELENIUM IN THE PLANT

It is strange that of the thousands of plants analyzed for selenium there should be such a paucity of information on the selenium content of the different parts—the leaves, stems, flower, seed, etc. Beath, Eppson, and Gilbert (12) sepa-

rated the wheat plant into grain, stems and leaves, and roots. The stems and leaves contained about one-half to two-thirds as much selenium as did the grain and roots. The distribution varied in different samples, however, and it is difficult to arrive at valid conclusions from the data presented. Byers, Miller, Williams, and Lakin (27) found no difference in selenium content in the tops and roots of onions or sugar beets. Williams, Lakin, and Byers (208) reported about twice as much selenium in a sample of radish tops as in the roots in one case, and no difference in the second case. The selenium content of the first sample was much higher than that of the second. Taboury and Manceau (179) and Taboury and Coudray-Viau (178) have reported on the selenium content of mustard and rape, separated into roots, stalk, seed pod, and oil. The concentration in the seed pod was high in both species. Williams (205) has reported on the analysis of five samples of *Astragalus* and one of *Stanleya*. Although the separations of the plants into their parts differed in each case, the seed, with or without the pod, contained the highest concentration of selenium. With one exception, the leaves contained more selenium than the stem or the root. The flower also contained relatively large quantities of selenium.

Hurd-Karrer (85) made the rather interesting observation that the relative distribution of selenium between the roots and tops of the wheat plant depended on the source of selenium. Plants supplied with a selenite contained a higher percentage of selenium in the roots than in the tops. The reverse condition was obtained for plants supplied with selenate. Similar results were reported by Gile and Lakin (69). Hurd-Karrer (85) postulated that selenites are more easily reduced to elemental selenium than selenates in plant cells and, hence, transport to the leaves was retarded. The reduction did not occur when selenates were absorbed by roots. Johnson and Whitehead (94) reported on the distribution of selenium in the mature wheat plant in relation to the supply in the soil. At low levels of supply the concentration in the kernel and the stem was about equal. At high levels of selenium supply the concentration in the stem exceeded that in the kernel by substantial amounts. The lowest concentrations of selenium were found in the hull.

Somewhat more information is available concerning the distribution of selenium in milled seleniferous wheat. Robinson (153) reported in 1933 that the gluten of a toxic wheat contained 90 p.p.m. of selenium as compared to 11 p.p.m. in the whole wheat grain. Franke (57) reported in 1934 that the toxicant in toxic wheat and corn was carried in the protein fraction. A subsequent publication (60) indicated that the toxicant was selenium. In a later publication, Robinson (154) reported the following distribution of selenium in a toxic wheat (26 p.p.m. Se): gluten, 121

p.p.m.; bran, 22 p.p.m.; starch, 5 p.p.m., and soluble and suspended matter, 16 p.p.m. of selenium.

Thus, early in the attack on the selenium problem a keen interest developed in the natural plant compounds containing the element. Much effort was expended on the fractionation of proteins and the isolation of individual amino acids that might contain selenium as a substitute for sulfur. The possibility of such a substitution was first suggested by Cameron in 1880 (29). Painter and Franke (140) reported in 1935 that most of the selenium appeared to be in a compound very similar to cystine. However, their data indicated that selenium was not restricted to any one amino acid but was rather widely distributed throughout the protein fraction. Horn, Nelson, and Jones reported in 1936 (81) that the principal centers of the toxic selenium compounds were the proteins gliadin and glutenin. Upon hydrolysis it was found that the leucine fraction contained most of the selenium. In a later publication (95) it was reported that peptized gluten adjusted to pH 6.2 and with the precipitate removed the gluten contained most of the selenium and was high in cystine. In further work, Horn and Jones (80) isolated and crystallized from *Astragalus pectinatus* an amino acid complex containing both selenium and sulfur and agreeing in chemical properties and composition to the following isomorphous amino acids:  $\text{HOOC}-\text{CH}(\text{NH}_2)-\text{CH}_2-\text{Se}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{NH})-\text{COOH}$ , and  $\text{HOOC}-\text{CH}(\text{NH}_2)-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{NH})-\text{COOH}$  in the ratio of 2:1. The amount of selenium contained in the isolated crystalline material represented only a small part of that contained in the total plant material.

The knowledge that wheat grown in seleniferous areas would absorb selenium and accumulate it in the grain led to several studies of wheat byproducts and flour, particularly since public health might be involved. Robinson (154) examined samples of flour from Maryland and North Dakota. Both contained a minimal quantity of selenium. Lakin and Byers (100) and Williams, Lakin, and Byers (209) reported on a large number of samples of flour and wheat byproducts, all obtained from Western United States. Of 66 samples of flour only 5 contained selenium in excess of 1 p.p.m. and 3 samples contained 4 and 5 p.p.m. The samples of bran, shorts, and middlings ranged from 0.2 to 5 p.p.m., with no significant difference among the three fractions. These authors suggest that selenium may be present in small amounts in all wheat and wheat products.

Moxon and others (126) examined four samples of wheat grown in seleniferous areas of South Dakota. The selenium content of the grain ranged from 4.8 to 63 p.p.m. About 35 percent of the

selenium was found in the bran. The other fractions of the milled wheat did not vary materially from each other or the whole wheat grain in the concentration of selenium.

The inorganic forms of selenium in plant tissue have been investigated by Beath and Eppson (10). Although the method used for extracting the inorganic selenium compounds is empirical in nature, it represents a good means of accomplishing an approximation of such compounds. No selenate selenium was found in representative species of the seleniferous *Astragalus* and *Stanleya*, although a large portion of the selenium present was soluble in water. An examination of several native plants, including *Xylorrhiza* spp. and other selenium-indicator plants, showed that all contained large quantities of selenium as selenate. Only organic forms were found, however, in alfalfa, young wheat plants, and yellow sweetclover or in barley, corn, and oat grains.

These workers showed that species of *Astragalus* and *Stanleya* and possibly some forages and cereals were capable of converting selenate or selenite selenium entirely to organic compounds. The situation with respect to grasses was not so clear, however.

## EFFECT OF STAGE OF GROWTH ON SELENIUM CONTENT

Changes in the concentration of selenium as the plant matures have received only casual attention from most workers, whose primary aim has been to determine only the presence or absence of the element. Beath, Eppson, and Gilbert (12) reported some selenium values in plants of different size, but these authors have confounded size, stage of maturity, and age. Hence, some of their data are not interpretable. Other data (12, 127) indicated a smaller concentration in plants collected late in the fall than in young plants. As pointed out by Byers (23), an important criterion in the interpretation of field data is the variation that may be expected as a result of the age and stage of growth of the plant collected as the indicator of soil and animal nutritional relationships.

Moxon, Olson, and Searight (128) studied *Agropyron smithii*, *Aster multiflorus*, *Grindelia squarrosa* (Pursh) Dunal, *Melilotus officinalis* (L.) Lam., and several cereal plants. There was considerable variation in the trend of the selenium concentration as the plants matured, although in general it appears that the highest concentrations occurred in the very young plant. Johnson and Whitehead (94) have examined this problem further by growing wheat plants in soils containing different levels of selenium as sodium selenite. At low levels of selenium supply the more mature plants had a lower concentration of selenium than did their corresponding younger plants. The op-

posite trend occurred at high levels of selenium supply. At intermediate levels of supply little change occurred as the plant matured. In all cases there was a constant increase in the total uptake of selenium as the plant matured.

## EFFECT OF SELENIUM ON GROWTH OF PLANTS

The experience with indicator plants had suggested to several workers the possibility that selenium was essential to the growth of these plants. This supposition was based on the observation that such plants as certain *Astragalus* species, the *Stanleya*, and others were not found except on seleniferous soils.

Criteria for determining the essentiality of an element as generally accepted have been stated by Arnon (3) as follows: "The criterion of the foremost physiological significance is the requirement of an inorganic element for the successful completion of the life cycle of a plant. This is, of course, different from merely demonstrating a favorable effect on growth." Secondly, he states that it must be shown that this effect is peculiar to the specific element and that other elements cannot be substituted. And finally, according to Arnon, the direct effect of the element, as distinguished from its possible influence on the root environment, must be established. The toxicity of very low concentrations of selenium to certain plants had been reported in earlier work (29, 174, 192). Hence, the report of Levine (111) of an increased growth of lupin seedlings in a nutrient solution containing 1 to 10 p.p.m. of selenium was received with interest. According to this investigator, higher concentrations were toxic and the degree of toxicity was greatest when a selenite was used and lesser for a selenate. Hurd-Karrer (85) reported, however, that as little as 0.1 p.p.m. of selenium in nutrient solutions was toxic to the wheat plant when no sulfur was present in the nutrient solution, although her data indicated that this could be prevented by adding sulfur. Thus, with 192 p.p.m. of sulfur, injury was prevented when the concentration of selenium was as high as 16 p.p.m. Martin (118), however, was not able to confirm these observations. In his experiments 2.5 p.p.m. of sulfur in the nutrient solution prevented the toxicity of wheat plants caused by 1 p.p.m. of selenium, but even the highest levels of sulfur (80 to 640 p.p.m.) failed to counteract growth retardation at levels of 2 p.p.m. or more of selenium. In Martin's data the root development appeared to be stimulated by 1 p.p.m. of selenium and 2.5 to 5.0 p.p.m. of sulfur but not by higher levels of selenium at any level of sulfur. It was not shown whether or not quantities of selenium much smaller than 1 p.p.m. would have stimulated plant growth. In a later report, Hurd-

Karrer (87) claimed a growth stimulation in wheat seedlings with 4 p.p.m. of selenium as the selenate and 36 p.p.m. of sulfur in the nutrient solution. The difference in weight—0.65 vs. 0.71 gram—is hardly significant, however.

Quite different responses of *Astragalus* to selenium have been reported by Trelease and Trelease (189). Seeds of *Astragalus racemosus* containing 2,125 p.p.m. of selenium were germinated in sand culture and transferred to water culture. Seedlings that were given no added selenium made slow growth in comparison with those grown in a nutrient solution containing this element as selenite. In this experiment 81 p.p.m. of selenium was definitely toxic at all levels of sulfur. Additions of 1, 3, and 9 p.p.m. of selenium stimulated growth if 3 p.p.m. or more of sulfur were present, and the stimulation increased with increase of sulfur in the nutrient solution up to 81 p.p.m. Sodium selenite and potassium selenate were about equally effective as sources of selenium. In common with Hurd-Karrer's observations (88, 89, 90), the accumulation of selenium by the plant varied inversely with the concentration of sulfur in the nutrient solution. In a later report Trelease and Trelease (190) studied the response of an indicator plant *Astragalus racemosus* with *Astragalus crassicaarpus* Nutt., a nonindicator. Selenium as selenite was added to the nutrient solution in both cases. The two species of *Astragalus* responded entirely differently to selenium. The growth of *A. racemosus* was stimulated, whereas that of *A. crassicaarpus* was retarded as the quantity of selenium was increased. No marked difference in the accumulation of selenium by these plants was noted.

Perkins and King (143) have reported some effects on growth of wheat from additions of selenium to the soil. Levels of 0.4, 1.0, and 2.6 p.p.m. stimulated growth, whereas 6.4 p.p.m. was toxic. Stanford and Olson (173) have also noted some stimulation of growth in wheat, oats, and sorghum plants but not in corn plants as a result of adding 0.001 to 0.05 p.p.m. of selenium as sodium selenate to culture solutions. Sharrer and Schropp (159) reported that 1.3 p.p.m. of selenium in a culture solution containing 25 p.p.m. of sulfur was toxic to wheat, barley, and oats. No stimulation of growth was obtained with even extremely low levels of selenium. Corn, however, appeared to respond to concentrations up to 0.013 p.p.m. of selenium.

Stoklassa (174) showed in 1922 that 4 p.p.m. of selenium as selenite was slightly toxic to barley plants, but selenate at the same concentration was not. An indication that these concentrations of selenium accelerated growth in corn and buckwheat was reported. He also observed that radiation from radium seemed to accelerate the germination of all seedlings and to limit the toxicity of selenium as selenite. This effect of

radiation was also observed on plants growing in nutrient solutions with or without selenium.

It is obvious from the foregoing that Arnon's criteria (3) for essentiality of an element have not been met in any experiment cited here. In no case has the selenium-free seed been used. In fact, under the conditions described this would have been highly impractical to accomplish. In no case was the life cycle of the selenium-free plant studied, and it is obvious that there is a selenium-sulfur interaction either in the root environment or within the plant that prevents any interpretation of the evidence produced in these experiments of the effect of selenium alone. Hence, no evidence is available that selenium is an essential element for plant growth even for the selenium indicator plants such as the *Astragalus* species.

## MISCELLANEOUS FACTORS AFFECTING THE ABSORPTION OF SELENIUM BY PLANTS

The effect of sulfur in inhibiting the absorption of selenium by wheat has already been discussed. In 1937 Beath, Eppson, and Gilbert (12) reported that decomposed seleniferous range plants (indicator and converter plants) were the chief source of selenium to farm crops. They claimed that these latter crops were incapable of absorbing enough selenium from seleniferous shales to become toxic. In greenhouse experiments Trelease and Di Somma (186) found that corn seedlings absorbed and accumulated from 5- to 14-fold more selenium from the organic compounds in a water extract of seleniferous *Astragalus bisulcatus* than from a sodium selenite solution of equal selenium concentration. Furthermore, a marked increase in the accumulation of selenium from sodium selenite occurred after the addition to the nutrient solution of an extract of dried, ground non-seleniferous string beans. The nonseleniferous plant extract appeared to have a protective action to the corn seedlings against selenium toxicity.

Further work by Trelease and Greenfield (187) indicates that several proteins and amino acids added to the nutrient solution will enhance the uptake of selenium by the corn plant. These authors suggest that inorganic selenium is less toxic when entering the plant in company with these organic compounds than when entering alone.

Taboury and Coudray-Viau (178) have studied the effect of selenium in the nutrient culture on the absorption of a number of elements by mustard and radishes. The data indicate that the concentration of iron, manganese, magnesium, and lithium is higher in the normal plant than in the seleniferous plant. Calcium, strontium, and barium were lower in the normal plant.

# Use and Limitations of Selenium as an Insecticide

By FLOYD F. SMITH

Selenium compounds as possible insecticides were first investigated by Gnadinger in 1933 (71). Selenium was investigated because of its close relationship to sulfur, one of the better miticides available at that time, and because these two elements form analogous compounds. The compound best suited for mite control on greenhouse plants was formed by dissolving selenium in potassium ammonium sulfide solution in proportions corresponding to the formula  $(K(NH_4)S)_5 Se$ . A 30-percent solution designated as Selocide at a 1 to 200 dilution with a soap spreader destroyed *Tetranychus telarius* L. on greenhouse plants, also *Paratetranychus citri* McG. and *Phyllocoptes* spp. on citrus in the field. At 1 to 800 dilutions it killed 95 percent of *T. pacificus* McG. on grapes. In further tests with *P. citri*, Selocide was used at 1 to 600 dilution in combination with spreaders and with lime-sulfur and a light spray oil with blood albumen emulsifier. The highest kill obtained was with the oil combination, which destroyed over 99 percent of the older mites but which was less effective against the eggs.

Gnadinger (71) discussed the toxicity of selenium-spray residues and considered the toxic action of selenites and selenates to be similar to that of arsenites and arsenates. He further pointed out that Selocide in a spray at a dilution of 1 to 500 contains only one-fifth the quantity of selenium as compared to arsenic found in the standard lead arsenate sprays then in use. Furthermore, Selocide would be applied only once or twice a year as compared to the usual four to nine applications of lead arsenate. He considered selenium residues from such a schedule to be less dangerous than residues from arsenical sprays in an established program.

The reports by Nelson and others (136) in 1933 and White (203) in 1934 pointed out the dangerously poisonous qualities of selenium compounds as discussed later under Health Hazards (p. 45). This, no doubt, influenced the thinking of subsequent research workers on the limitations of this insecticide.

Boyce (20) in 1936 found Selocide at 1 to 800 dilution to be the most promising material other than oil sprays for red mites on citrus. He found the effectiveness was increased by addition of lime-sulfur (1 to 300), wettable sulfur (2 lb./100 gal.), or light mineral oil (1 to 300). The selenium-sulfur compounds killed only those eggs in which the embryo was well developed, but the residue on foliage destroyed young hatching mites. The Selocide-oil combinations gave high initial kills of mites but lacked the residual effect.

After Hoskins (82) found residues of selenium in fruits of treated grapes and citrus, Boyce and Prendergast (21) considered it inadvisable to use selenium substances on citrus and discontinued further studies with this compound in California.

Taylor (181), reporting on investigations in New Zealand, found Selocide more effective against *Paratetranychus pilosus* C. & F. than HETP, TEPP, Parathion, or karathane. One or two sprayings after blossoming gave protection for most of the season. Analyses of the fruits indicated selenium residues of 0.3 p.p.m. or less. However, he pointed out that a diet containing 3 p.p.m. could be consumed without ill effects.

Compton and Kearns (38) in 1937 found that *T. telarius* mites on rose were much harder to kill than on snapdragon, which may be the first report of resistance in this species. These authors found that by use of a wetting agent such as Aresket 240 a 1-percent Selocide solution, was equal to a 2-percent solution without a wetting agent.

In the investigations reviewed above the nature of the insecticidal action of selenium in Selocide was not discussed. It was compared with other insecticides on the basis of immediate kill and residual action. In 1936 Hurd-Karrer and Poos (91) first demonstrated that selenium was a systemic insecticide in plants. They showed that selenium was absorbed by the roots of wheat plants from the substrate and translocated to the foliage where it killed aphids (*Rhopalosiphum prunifoliae* Fitch.) at concentrations too low to cause visible effects on the plants themselves. The aphids did not distinguish between treated and untreated plants in their feeding preferences. Thus, a purely physiological study provided the suggestion for a fresh approach to pest control on plants.

Luekel (109) in 1940 protected sorghum plants in the greenhouse from attack by *Aphis maidis* Fitch and *T. telarius* by applying water solutions of sodium selenate at the rate of 4 p.p.m. by weight to the soil. Lower dosages at 2 or 3 p.p.m. were ineffective, and higher dosages 5 to 15 p.p.m. stunted the growth.

In 1940 Neiswander and Morris (135) added sodium selenate to nutrient solutions in which chrysanthemums were growing; at a 2-p.p.m. rate the concentration in the leaves was 45 p.p.m., which eliminated *Macrosiphoniella sanborni* (Gill.); and at a 4-p.p.m. rate the foliage contained 90 to 100 p.p.m. selenium, which destroyed *T. telarius*. Tomato plants growing in solutions containing 1.5 p.p.m. selenium concentrated sufficient selenium in the leaves to kill *T. telarius*. Carnations required 6-p.p.m. concentrations in



the soil to kill mites; they failed, however, to absorb toxic amounts of selenium when grown in nutrient solutions. Roses growing in solutions containing 0.5 p.p.m. selenium were defoliated by mites but at a 2.5-p.p.m. level they were protected from mite attack and grew well.

Speyer and coworkers (172) found that insufficient selenium was taken up by tomato seeds soaked in sodium selenate solutions for 24 hours before sowing to immunize the seedling plants from attack by *T. telarius*. Seedling tomatoes grown in soil or compost containing more than 50 p.p.m. of sodium selenate were severely injured. Plants grown in soil at lower levels of selenate were immunized from mite attack, but plants grown from seed from these treated plants were severely damaged by mites. These authors pointed out the risk of rendering tomato fruits unsuitable for consumption and of the contamination of the soil for other crops.

English (50) prevented attack of aphids, spider mites, and the Mexican mealybug (*Phenacoccus gossypii* T. & C.) on chrysanthemum and of spider mites and grape mealybugs (*Pseudococcus maritimus* Ehrh.) on carnation by a single 0.25 gram dosage per square foot of soil application of sodium selenate. Five varieties of chrysanthemum tolerated the treatment but a sixth one was injured. Carnation shoots were stunted, but flower production was not reduced. Farrar (52) found that vigorously growing chrysanthemum plants tolerated higher dosages of sodium selenate in the soil than did weak-growing varieties; also that mites, mealybugs, and thrips were destroyed by the standard dosage of 0.25 gram per square foot, but not the chrysanthemum midge as reported by Blauvelt (19). In field trials a 0.25-gram dosage per square foot of soil controlled gladiolus thrips (*Taeniothrips simplex* Morison). In 1945 Blauvelt (19) published the first practical recommendations for applying sodium selenate, in solution or impregnated on pelleted phosphate rock, to the soil of greenhouse flowering crops for the control of spider mites and aphids on chrysanthemums and carnations; chrysanthemum midge (*Diarthronomyia chrysanthemi* Ahlberg) and foliar nematodes on chrysanthemum; and cyclamen mite (*Steneotarsonemus pallidus* (Banks)) on chrysanthemums and African-violets. His procedures for application and his dosage rates for various crops are still used.

## TOLERANCE OF INSECTS TO SELENIUM

Of the insects tested, aphids were probably the most susceptible to selenium in plants. On chrysanthemums in nutrient solutions containing sodium selenate, *Macrosiphoniella sanborni* and *Petranychus telarius* were killed by leaf concentrations of 45 p.p.m. and 90 to 100 p.p.m., re-

spectively. Tests by Morris and coworkers (122) in 1941 showed that *Aphis maidis* Fitch did not survive on corn plants containing 25 p.p.m. of selenium. On other plants with selenium content of 50 p.p.m., occasional sluggish *T. telarius* mites were found, and at 100 p.p.m. all mites were killed. That mites can change in their susceptibility was indicated by Quayle (146), who reviewed the increased resistance in insects to insecticides and stated that Selocide had ceased to be effective against *T. telarius* in greenhouses of Eastern States, although it was of outstanding value for a few years.

Fox (56) reported on the tolerance to and possible preference for high levels of selenium by several species of insects in their choice of food plants. *Astragalus pectinatus* (Hook.) G. Don (*Cnemidophacos pectinatus* (Dougl.) Rydb.), a milkvetch growing in selenium-bearing soils in Saskatchewan, contained 58 to 969 p.p.m. of selenium in the roots and 162 to 4,190 in the foliage; another vetch (*A. bisulcatus* (Hook.) Gray (*Diholcos bisulcatus* (Hook.) Rydb.)) contained as much as 3,640 p.p.m. A Cerambycid *Anonlo-dera instabilis* Hald. and the Tineid *Walshia amorphella* Clem. bred in the roots of both of these vetches. Larvae of *A. instabilis* occurred in roots of *A. pectinatus* containing 154 to 969 p.p.m. selenium, whereas the selenium content of roots of uninfested plants contained only 58 p.p.m. Other insects that fed on the nearby roots of these plants included larvae of *Corymbites* (*Ludius aeripennis destructor* Brown, *Drasterius* (*Aeolus*) *melillus* Say, and *Brachyrhinus ovatus* L. Three Meloids fed on the foliage of both species, and *Bruchus seminulum* Horn and a Eurytomid near *Bruchophagus gibbus* Boh. occurred in the seeds of both.

Other studies in Wyoming (188) showed that *Bruchus fraterculus* Horn completed its life cycle in seeds of *Astragalus bisulcatus* that contained 1,475 p.p.m. selenium; also that two parasites *Bruchophagus mexicanus* Ash. and *Eutelus bruchophagi* Sah. were present.

In experiments by Bennett and Martin (17) in 1948 mature grain from wheat plants grown in soil treated with sodium selenate was infested with adult granary weevils (*Calandra granaria*). The grain was not toxic to the adults, but no eggs or larvae developed in the infested seeds. The absence of eggs suggests the possibility that certain vitamins or proteins containing sulfur are concerned in the reproductive process and that these become deranged in the presence of analagous selenium compounds (17).

## COMPATIBILITY WITH OTHER INSECTICIDES

As mentioned earlier (18, 71, 83), several workers found increased kill of mites and insects when lime-sulfur, wettable sulfur, or light spray oil

were combined with the Selocide. Selocide was also compatible with nicotine sulfate, zinc oxide, and zinc sulfide, but not with zinc sulfate and hydrated lime (82).

In 1936 Lilly (113) obtained increased kills of the cherry case bearer (*Coleophora pruniella* Clem.), the bud moth (*Eucosma ocellana* Schiff.), and the fruit tree leafroller (*Tortrix argyrospila* Wlk.) by adding Selocide to the usual dormant oil sprays applied for control of these apple pests.

Hoskins reported (82) in 1938 that Selocide (1 to 800) in combination with a medium oil in emulsion successfully controlled *Paratetranychus citri* and *Tetranychus sexmaculatus* Riley; and Selocide plus wettable sulfur controlled citrus thrips *Scirtothrips citri* Moul. and *Phyllocoptruta oleivorus* Ashm. Results of comparative tests with Selocide alone were not included.

Taylor (181) reported that adding sulfur to Selocide sprays had a synergistic effect, but that in combinations with lead arsenate Selocide severely damaged foliage.

Fuller (65) obtained excellent control of aphids on chrysanthemum with 0.2-gram dosage of sodium selenate in dry mixtures with limestone but obtained only partial control with gypsum. However, best aphid control and least plant injury was obtained with 0.4-gram dosage of sodium selenate in gypsum. Plant analysis indicated that gypsum reduced plant absorption of selenium and of toxicity to the aphids, probably owing to the available sulfur content of the gypsum. Moxon (125) pointed out that grasshopper damage was equally severe in seleniferous and nonseleniferous soils of South Dakota. A direct correlation occurs between the selenium content of the grasshoppers and that of the vegetation upon which they fed. Because arsenic is rendered more or less non-toxic by selenium, Moxon believes the effectiveness of arsenic for poisoning grasshoppers in seleniferous areas is questionable.

## KINDS OF PLANTS TREATED

In 1941 Morris and coworkers (122) prevented attack of *Tetranychus telarius* on young apple, elm, legumes, and wheat plants growing in sand or soil cultures by adding sodium selenate at rates of 1 to 10 p.p.m.

Wolfenbarger (210) reported that Selocide sprays on avocado and mangos were ineffective against *Paratetranychus yothersi* (McG.) in Florida.

## FORMS OF SELENIUM INSECTICIDES

Sodium selenate as crystals and usually dyed blue or red is available in bulk to florists and nurserymen who make up solutions for soil drenches.

Capsules containing one-fourth gram of sodium selenate are packaged for shipping through the mails or for sale in seed stores and garden supply houses. They are mostly used in the home or small greenhouses for the control of cyclamen mites on African-violets or other plants. Each package of capsules is accompanied by directions for preparing sodium selenate solutions and the quantity to be used for each plant according to the size of the pot. Four capsules containing a total of 1 gram of the chemical will make 1 gallon of solution, which is sufficient for 64 4-inch pots or 256 2-inch pots.

Capsules of sodium selenate diluted with an inert carrier are also available for a one-capsule-per-plant treatment. Lindane is added by some firms to provide a combined foliage and soil insecticide.

Specialty prepared phosphate rock, in pellets and treated with a hot solution of sodium selenate to give a 2-percent sodium selenate content, is packaged in 25- to 100-pound drums for sale to florists. The material is broadcast over the soil surface at rates of 1½ to 3 pounds per 100 square feet to give an approximate application rate of one-eighth to one-fourth gram per square foot.

Selocide containing 30 percent potassium ammonium selenosulfide has been the most widely used selenium formulation for foliage sprays.

Schrader (160) synthesized compounds of phosphorus and selenium—including diethyl ethylmercaptoethyl selenophosphate, a selenium analog of demeton—which were toxic to insects. However, Schrader found all of his analogs had unpleasant odors, were expensive to produce, and were highly toxic to warm-blooded animals. None have been made commercially.

Anthony (2) obtained complete control of the black cherry aphid (*Myzus cerasi* F.) on cherries and the green peach aphid and spider mites on peach by foliage sprays containing 1.2 ounces of Schrader's selenium analog in an emulsion concentrate.

In studies by Kiplinger and Fuller (96) selenates of copper or potassium were more toxic to aphids than were selenates of calcium or sodium.

## METHODS OF APPLICATION

*Soil applications.*—To be successful with sodium selenate as a systemic poison, rather exacting conditions must be observed to attain the desired concentrations in the plant for insect kill and to avoid excessive quantities that would be phytotoxic. In practical applications of sodium selenate to soil in greenhouse benches, plant-growth conditions conducive to uniform translocation enhance the systemic action. Best kills are obtained on vigorous, young, well-established plants.



Young seedling plants are more susceptible to injury, and selenium uptake in older plants or in those injured by insects or mites is sometimes too slow to be effective. Thus, Kiplinger and Fuller (96) obtained no control of mealybugs on gardenia, a woody-stemmed plant, or on the fleshy-stemmed *Begonia socotrana* Hook. f., apparently because of its extreme susceptibility and leaf drop. Also aphids and spider mites were controlled by soil applications of sodium selenate on tender current season growth of recently propagated hydrangea, but no control was obtained on older woody-stemmed plants.

Treatments are not made when temperatures are excessively high, because of increased transpiration rate and the buildup of phytotoxic concentrations of selenium in the leaves. Treatments during November through January are avoided, because selenium uptake is slow during the short winter days. The ill effect of overdosage can be corrected by leaching the soil with water and by applications of gypsum or sulfur.

The danger of plant injury from a single  $\frac{1}{4}$ -gram application is reduced by making two applications of sodium selenate at a  $\frac{1}{8}$ -gram rate in solution or in fertilizer mixture, with a 4- to 6-week interval between applications.

One series of treatments is required for short-term crops such as chrysanthemums, but carnations are usually treated at 6-month intervals to replace the selenium taken up by the plants lost through leaching or chemically transformed in the soil.

*Foliage applications.*—Selocide containing 30 percent potassium ammonium selenosulfide has been the most widely used formulation for foliage sprays on citrus and apple trees and was used on roses and other greenhouse crops until resistance of mites developed. The usual application rate is 1 pint per 100 gallons. Foliage applications of Selocide appear to have short residual action and systemic qualities are not shown as exhibited by selenium in soil applications.

## QUANTITY MARKETING

Although a large number of individuals who grow ornamentals benefit from selenium in its various forms for insect control, the total quantity of selenium compounds actually marketed as insecticides is small.

One small-scale formulator indicated approximately 2,000 annual mail order sales of sodium selenate in 25,000  $\frac{1}{4}$ -gram capsules, chiefly to growers of African-violets for cyclamen mite control. He requires approximately 14 pounds of the chemical to fill these orders. The same formulator has an increasing demand for capsules containing

lindane plus 1.3 percent sodium selenate for use as a capsule-per-pot treatment. Larger concerns have made wide distribution of diluted sodium selenate in capsules for treating individual pots through retailers of seeds, flowers, and garden supplies.

There is a small but steady demand by florists for bulk crystalline sodium selenate for application to the soil as a water solution to control spider mites, aphids, and certain foliar nematodes; also for the phosphate fertilizer-selenate mixture in 25- to 100-pound drums for broadcast applications. The florists' demand for selenium in Selocide for use as foliage sprays has practically ceased, because of its failure to control resistant spider mites.

Information is not available on the quantities of sodium-selenate or Selocide used in sprays on citrus or other crops in California, the only State in which seleniferous insecticides have been registered for use on food crops.

## DANGERS OF TREATED PLANTS AND SOILS TO ANIMALS

Plants take up varying amounts of selenium from the soils in which they grow. Food plants grown in naturally seleniferous soils or in soils treated with selenium compounds for pest control are a threat to the health of man or animals ingesting them.

Hurd-Karrar (88) reported that plants with high sulfur requirement also store relatively large quantities of selenium. Such crops are broccoli, cabbage, cauliflower, mustard, and onions.

Kiplinger and Fuller (96) found that the uptake of selenium in chrysanthemum plants varied with the rate of soil application of sodium selenate; at a  $\frac{1}{8}$ -gram-per-square-foot application an equilibrium of 70 p.p.m. was reached in 3 weeks, whereas with  $\frac{1}{4}$ - or  $\frac{1}{2}$ -gram applications the uptake in the plant increased for about 7 weeks to an equilibrium of 425 or 690 p.p.m., respectively.

When the workers added sodium selenate in nutrient solution to corn plants at 2-week intervals at rates ranging from 0.5 to 3 p.p.m., they found selenium contents of the foliage ranging from 25 to 150 p.p.m., respectively (122).

Fuller (64) investigated the selenium content of vegetables grown on greenhouse soils treated with sodium selenate. Carnations were grown in the soil and treated with sodium selenate at the rate of 0.25 gram per square foot. The carnations were removed 7 months later and vegetables planted. Leaf lettuce and onions from sets planted in the same soil contained 0.24 and 3.4 p.p.m. selenium, respectively, when harvested. In another experiment lettuce contained 4.2 p.p.m.

selenium at harvest when it followed a chrysanthemum crop that had been grown in soil treated with 0.5 gram of sodium selenate per square foot. In these experiments the selenium content available to plants was depleted only by reaction with soil and by the growing chrysanthemums; it was not leached out by excessive watering or other treatment. Cabbage and onions contained 6.1 and 5.6 p.p.m. of selenium, respectively, when grown in soil treated with 0.5 gram sodium selenate per square foot, then kept fallow for 6½ months without watering until planting time.

Fuller (64) also conducted experiments to deplete the selenium contents of the soil or inhibit the selenium uptake. Lettuce grown in soil treated with one-fourth gram of sodium selenate per square foot (or 24 lb. per acre) after the crop was established contained 35 p.p.m. of selenium at harvest. Lettuce planted in similarly treated soil that was leached with water at 2½ or 5 gallons per square foot before planting had a selenium content of 13 and 2 p.p.m., respectively. A 2½-gallon leach per square foot plus 10 pounds of gypsum or 2 pounds of sulfur per 100 square feet reduced the selenium content in the succeeding lettuce crop to 3 and 1 p.p.m., respectively. Fuller (64) concluded that drastic leaching alone or moderate leaching plus addition of sulfur or gypsum offers an effective method for reducing danger of selenium in food crops grown on soils previously treated with sodium selenate.

## HEALTH HAZARDS FROM SELENIUM RESIDUES

In a summary of spray residue problems in 1934, White (203) stated that care is needed in the exploitation of new potentially dangerous insecticides such as those containing selenium.

In 1933 Nelson and others (136) warned against the use of selenium as an insecticide. Quantities as small as 1 p.p.m. in the soil permitted growth and maturation of wheat, but when the grain that contained 8 to 10 p.p.m. selenium was fed to rats and guinea pigs it retarded their growth and death followed after a few weeks. These authors further stated that selenium can be absorbed from the soil by at least some and possibly all plants. Even the complete removal of surface-spray residue from an edible product might be no safeguard; and the degree of toxicity of the compound used in spraying is not a measure of the toxicity of the compounds formed in the plant. Moreover, there is evidence that selenium compounds may be reduced by soil organisms, so that spray residues ordinarily considered innocuous may be

made available to the plant and be converted to highly toxic combinations.

In 1938 Hoskins (82) found residues of 0.6 p.p.m. selenium in fruits of vinifera grapes from plots sprayed for several years with Selocide at 1 to 600 dilution for control of *Tetranychus pacificus* McG. The residues were less when the sprays had been applied in previous years only.

In tests on citrus fruits from trees sprayed with Selocide at 1 to 800 dilution, Hoskins (82) also found residues of 0.21 and 0.06 p.p.m. in the skin and pulp, respectively, whereas the corresponding parts of untreated fruits averaged 0.10 and 0.05 p.p.m., respectively. The selenium content was 0.25 p.p.m. in untreated soils and was always less than 1.0 p.p.m. in soils of plots treated up to 6 times.

In New Zealand Taylor (181) stated that the maximum amount of selenium in the whole diet that man can consume without ill effects is believed to be 3 p.p.m. He reported that analysis of apples at harvest showed less than 0.08 p.p.m. selenium in fresh fruit from trees sprayed twice with 1 pint of Selocide per 100 gallons 4 months previously. He found 0.3 p.p.m. in fruits sprayed 1 or 2 months before harvest; and fruit from unsprayed trees contained 0.04 p.p.m. No evidence was obtained of any tendency for apple trees to assimilate increased amounts of selenium after having been sprayed for three successive years with Selocide.

Fuller (64) and Kiplinger and Fuller (96) found 0.24 p.p.m. selenium in fresh lettuce and 3.44 p.p.m. in green onions, or 3.8 and 31.3 p.p.m. respectively on dry-weight basis. They state that the best estimate they can get is from a study of the U.S. Public Health Reports by Smith and associates (167, 168, 169, 170). They also reported that a daily intake of 1 mg. of selenium in food is probably not harmful to an adult person. On this basis 0.5 lb. of any vegetable that contains not more than 4.5 p.p.m. of selenium would be entirely safe for normal inclusion in the daily diet, provided that other constituents of the total food supply were not seleniferous.

In a later paper Fuller (66) points out that by adding sodium selenate to the nutrient medium of some ornamental crops they can be protected from attack by certain pests. He emphasized that selenium or its compounds should in no case be used on crops which may ultimately be used as food for humans or domestic animals or on land that might be used for growing such crops. This is in keeping with the present recommendations for use of selenium; it has a zero tolerance on all food crops and has been registered for use only on ornamentals, except for the registered use on citrus in California.

## Effect of Selenium on Animals

By E. J. THACKER

The effects of selenium on animals have been discussed in the comprehensive reviews by Moxon and coworkers (122, 123, 127) and in the original description by Franke and associates (59, 62). Moxon and Rhian (131) state "The chronic type, 'alkali disease' is predominant in South Dakota and in other States where seleniferous soils are formed extensively. It results from the consumption of vegetation, grains and forages containing up to approximately 25.0 p.p.m. of selenium for a period of several days or weeks." Dullness and lack of vitality is a general symptom. The animals become emaciated, stiff, and lame, and fail to respond to good care and selenium-free feed. A prominent symptom in horses and mules is the loss of the long hair from the mane and tail. This loss often takes place within a month after horses are moved to seleniferous areas.

"The loss of long hair from the mane and tail in horses and mules, and the loss of the long hair from the switch of cattle is usually accompanied

or followed shortly by lameness and soreness of the feet [fig. 8]. Swelling appears at the coronary band. In very mild cases there may be no further change although the animals may be lame for some time. In severe cases a gradual separation of the wall of the hoof occurs below the coronary band, and a new growth of hoof starts at the coronary band. In some cases the old hoof is sloughed off and in others it remains attached to the new growth until the new hoof has grown to normal length. In cattle the old hoof usually remains attached to the new growth and in cases where there have been several attacks the old ragged hoofs may be 8 or 10 inches long and turned upward at the end [fig. 9]. During the time the animals are sloughing the old hoofs and growing new ones they are very lame and often are in severe pain. Usually they do not move about much and unless feed and water are within easy reach, death may result from starvation and thirst."



Figure 8.—Selenized animals frequently rest on their knees to relieve the pain of standing on sore, deformed feet.



*Figure 9.*—Severely selenized cattle frequently lose portions of their hoofs and the general body condition becomes severely emaciated.

"In hogs the symptoms of 'alkali disease' are emaciation, lameness, loss of hair from the body and irregular growth of the hoofs with occasional sloughing of the hoofs similar to the condition in cattle and horses [fig. 10]. When young pigs are fed corn containing 10 p.p.m. to 15 p.p.m. of selenium, the symptoms appear within 2 or 3 weeks."

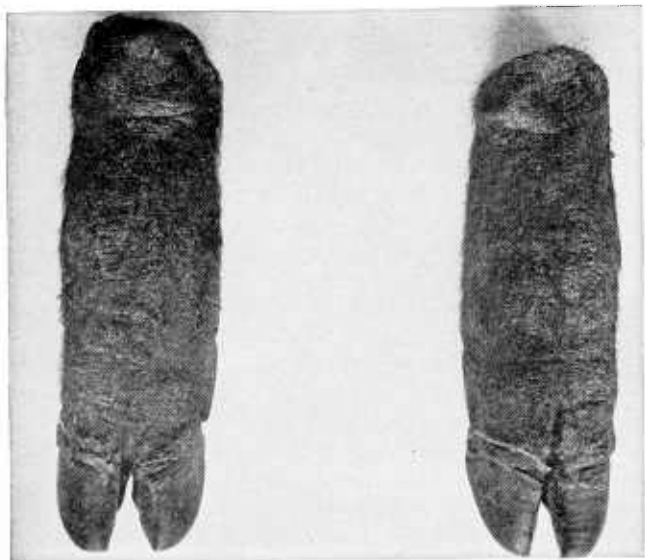
In Wyoming a more acute type of selenium poisoning has been observed. Beath and co-workers (8) state: "The animals, particularly cattle, exhibit early in the stage of poisoning a dullness and a lack of vitality. It is evident early in the stage of poisoning that there is a stasis of the gastrointestinal tract. There is considerable abdominal pain, with grunting, grating of teeth and salivation. Shortly before the paralytic stage animals exhibit excitement, with a tendency to constantly wander, often aimlessly in circles. The animal may or may not show impairment of vision. Prior to death the animal exhibits varying degrees of paralysis, which becomes serious when it involves the swallowing mechanism."

Pathologically, the lesions of selenium poisoning may be those of an acute, subacute, or chronic reaction. Acute poisoning was experimentally produced by Miller and Williams (120) in the horse, mule, cow, and swine, and death followed within hours the administration of lethal doses of selenium as sodium selenite. These authors described the clinical symptoms of an acute toxicity in horses as follows: "There is first a lack of appetite and refusal to drink water, and the animal

stands quietly in the stall. The pulse is slightly accelerated and the respirations are fast. The temperature may be normal or slightly higher. A few hours before death, the animal stands as though fixed to the floor, eyes staring, nostrils dilated, and the breathing is convulsive, fast, and very labored. The temperature has a tendency to rise, and the pulse is fast and weak or imperceptible in some animals. A blood sample taken at this time is almost black in color, but there is no hemolysis."

Necropsy revealed small, black hemorrhages, few in number, on the surface of the lungs and visceral pleura, along the coronary groove, and on the pericardium, with multiple hemorrhages under the endocardium extending into the myocardium. Subcapsular hemorrhages were noted on the spleen and kidney, and the kidney was soft and friable. Severe gastritis and enteritis were present, frequently with ulceration. Cloudy swelling, fatty degeneration, and small hemorrhagic areas indicated liver injury. Acute nephritis and cortical hemorrhages were seen, as well as cystitis, which was manifested as a diffuse, ulcerative or catarrhal lesion. Death in acute poisoning probably follows a marked reduction in the respiratory capacity of the blood or asphyxiation (11).

The pathology of "blind staggers" is characterized by the presence of acute and chronic lesions, with death attributed to physiological anoxia.



**Figure 10.**—The lower portion of hogs' legs frequently lose hair, and the hoofs show a gradual separation of the walls below the coronary band.

The following description is paraphrased from Draize and Beath (45) and Rosenfeld and Beath's study (157) of this disease. Acute congestion, hemorrhages, and fibrosis were grossly evident in the lungs. Fibroblastic proliferation, lymphocytic infiltration, hemorrhages, and edema thickened the alveoli walls to the extent of alveoli obliteration. The heart was atrophied and fibrotic, with all layers showing hemorrhages. On section fibrosis, congestion and necrosis, with a serofibrinous exudate around the coronary vessels, were observed.

The principal pathological changes in the liver were varying degrees of fatty degeneration, necrosis, and early fibrosis. Large amounts of fat, bile duct proliferation, necrosis around the central vein, and initial fibrotic changes destroyed the normal architecture of the liver. The gastrointestinal tract showed desquamation of epithelium, congestion, hemorrhage, and frequently ulceration of the stomach mucosa.

In the kidney, the cortical-medullary boundary was indistinct and contained petechial hemorrhages. Microscopically, glomerulonephritis and tubular changes were evident. Endothelial proliferation, fatty infiltration, and epithelial crescents were noted in the glomeruli and coagulation necrosis of the tubules. The spleen tended to be enlarged and firm with the cut surface mottled with red and grayish-red areas. The sinusoids were dilated and the pulp appeared congested with red blood cells. Many malpighian corpuscles appeared hyperplastic. Reticular fibrosis and thickening of the trabeculae and of the blood

vessel walls were evident. Congested and hemorrhagic lymph nodes also showed fatty and variable fibrotic changes. The reproductive organs were congested. In some animals necrosis and edema were observed in the anterior pituitary.

No specific pathological lesion has been associated with the apparent impairment of vision observed in many cases of "blind staggers." Since blood plasma vitamin A levels are reduced in subacute selenium poisoning (156), the suggestion was advanced that the impaired vision was a result of a physiological vitamin A deficiency. Confirmatory evidence for this has not been reported. The apparent blindness may be a manifestation of physiological anoxia associated with the acute phase of the toxicity.

The pathologic changes observed in "alkali disease" reflect the progressive degenerative changes of chronic selenium toxicity. Swelling and inflammation of the hoof coronary band and the possible erosion of the articular surface of the long bones would explain the painful lameness seen in this condition.

The heart was soft, flabby, and atrophied, with obvious areas of myocardial fibrosis. Microscopically, muscle fiber atrophy, myocardial fibrosis, edema, and foci of lymphocytic infiltration were noted. The normal histological structure of the lung was destroyed by the atelectatic interstitial tissue and fibroblastic proliferation. Liver damage was pronounced, with the normal lobule architecture of the liver disturbed by a fibrotic replacement of the parenchymal tissue. Typical portal cirrhosis was seen in the advanced cases.

Atrophy, hyaline degeneration, and tubular calcification were seen in the kidneys, with increased interstitial tissue, fibrosis, and thickening of the blood vessel walls. In the spleen the reticulum and trabeculae were proliferated, and the Malpighian corpuscles may be either hyperplastic or fibrotic. The testes and ovaries were atrophied and fibrotic.

A polioencephalomalacia (forage poisoning) in feedlot and pastured cattle and sheep has been reported (93) from Colorado in which the clinical symptoms were identical to those ascribed to blind staggers in Wyoming. The significant lesions were limited to the brain in which foci of necrosis were observed throughout the cerebral cortex. The condition was demonstrated to be noncontagious. Attempts to reproduce the disease by feeding vegetation and water collected from the areas associated with the disease were unsuccessful. Analysis of tissues from the afflicted animals indicated a variable selenium content.

The cause of forage poisoning is unknown and, in the absence of information on the possible brain damage in the blind staggers of alkali disease, the



relationship of forage poisoning to blind staggers is uncertain.

Maag, Orsborn, and Clopton (115) have recently reported from Colorado an experiment in which an attempt was made to develop chronic selenium poisoning by feeding an inorganic source of selenium for periods extending for 28 weeks. Sodium selenite was fed by capsule to 8 steers at the rate of 0.25 to 0.50 mg. selenium for each pound of body weight three times a week. No symptoms of poisoning were evident when selenium was fed at a rate that resulted in a selenium blood level of 3.0 p.p.m. or less. Symptoms of toxicosis were observed when blood levels exceeded 3.0 p.p.m. and inappetence and depression of the animals appeared when blood selenium exceeded 4.0 p.p.m. Polioencephalomalacia was observed clinically and confirmed pathologically in two steers fed selenium for 8 and 22 weeks. Rumenitis, abomasitis, and enterocolitis were noted in six steers that died during the experiment. Two animals slaughtered after 28 weeks were free of lesions attributable to selenium. Prolonged feeding of inorganic selenium did not result in the steers exhibiting the classical symptoms of chronic selenium poisoning—deformed hoofs, lameness, roughened hair coat, shedding of the long hair, emaciation, or anemia. Whether or not the incidence of polioencephalomalacia in this experiment should be attributed to selenium feeding is equivocal.

The Colorado workers have effectively demonstrated that the prolonged ingestion of subacute quantities of selenium as an inorganic salt does not induce the syndrome attributed to chronic selenosis, which results when seleniferous plants are fed to animals. The etiological factors involved in the development of chronic selenosis or alkali disease would appear to be more complex than simple selenium intoxicification. Among the factors that may be involved are one or more of the alkaloidal constituents of certain seleniferous plants, specific organic compounds of selenium, and minor-element concentrations of unknown biological significance in the vegetation. These and other factors may be acting alone, together, or interacting physiologically in the animal to produce the syndrome of alkali disease presently ascribed to selenium poisoning. The apparently still obscure etiology of alkali disease presents a challenging problem for investigation in the interrelationships among the soil, plant, and animal as well as those of a metabolic nature, biochemical and physiological, essential to the etiological description of alkali disease.

Rosenfeld and Beath (157) have described a congenital malformation in a group of 250 lambs born in a band of 2,100 ewes grazed on a seleniferous area. Seventy-five percent of the malformed lambs died at birth and 10 percent died between

the ages of 3 to 5 months. The animals that survived showed a reduced rate of gain, thickened and nodular joints of the extremities, deformities of the eye, and hypoplasia of the reproductive organs. The gross and histological changes in the cystic malformed eyes were reported in detail. The eye abnormalities indicated that developmental arrest occurred early in gestation and the capacity for differentiation, growth, and proliferation was impaired or lost. Arrested growth, cellular proliferation, and lack of differentiation at certain developmental stages resulted in microphthalmia, rudimentary development, microcornea, and colobomas of the various structures. These observations have not been confirmed with experimental feeding of selenium.

Injury to poultry by ingestion of selenium has been extensively studied at the South Dakota Agricultural Experiment Station (123). Feed consumption and growth is reduced in the chick when the ration contains 8 p.p.m. selenium. As little as 3.5 p.p.m. in the ration of the hen results in the fertile eggs carrying deformed embryos. Eggs from hens fed selenized rations showed a poor hatchability. The chicks that do hatch are weak and carry a wiry and greasy appearing down (fig. 11). Fertility of the eggs was high, but hatchability was reduced by the high incidence of malformations. Many of the monster embryos died before the 21st day, others were unable to pip the shell because of a deformed upper beak. Other terata included microphthalmia, abnormal legs and wings, otocephaly, anencephaly, and any combination of these defects. The left side of the embryo was more severely affected than the right side (106).

A disease in wild ducks similar to the syndrome produced by *Clostridium botulinum* was believed by Towney and coworkers (194, 193) to be caused by selenium poisoning. However, Lakin, Quortrup, and Hotchkiss (105) were unable to confirm this from observations made in the vicinity of areas in which losses from western duck sickness were known to occur. Similar levels of selenium were found in livers of birds that died of botulism or that were shot in flight. The level of selenium in the liver was less than that reported as found in apparently healthy hens. The marsh vegetation and waters in affected areas were too low in selenium to be toxic. Furthermore, no deformities in young waterfowl in the affected areas were found. The possibility that fish in their native environment might be affected by seleniferous water is suggested by the work of Ellis, Motley, Ellis, and Jones (49). Goldfish kept in water containing 2 p.p.m. of selenium showed definite signs of toxicoses. A typical symptom was protruding eyes, loss of color or scales, incoordination with spasmodic movements.



**Figure 11.**—Selenized embryo chicks are frequently unable to pip the shell because of deformed beaks. The chicks also carry a wiry, greasy appearing down. Fertility of eggs may be high, but hatchability is low because of a high incidence of malformation.

## EXPERIMENTAL WORK WITH LABORATORY ANIMALS

The rat assay of toxicants in plant foodstuffs was reported by Franke in 1934 (57, 62), although it was not until a year later that he related the trouble to selenium. He found that elemental selenium added to the diet of the rat appeared to be harmless, whereas the different salts of selenium were about as toxic as a seleniferous wheat of equal selenium content. The symptoms were identical in all cases. In 1936, Munsell, DeVaney,

and Kennedy (133) reported on rat assays of a seleniferous wheat begun in 1931 after Robinson (153) reported the presence of this element in wheat. Unfortunately there is some confusion in the report of Munsell and coworkers (133), and it is not certain as to which rat in their paired-feeding experiment was fed the toxic grain. In further work these authors were able to establish that 0.25 milligram of selenium per 100 grams of body weight per week resulted in retarded growth, failure to reproduce, and the development of the characteristic symptoms of selenium poisoning. In view of recent findings (161, 162) it is interesting to note that Munsell and coworkers reported that the female rats of the first generation on the diet containing 0.75 p.p.m. of selenium and those of the second generation on 0.75 and 1.5 p.p.m. showed an apparent superiority over the control group in the number of young born and the percentage reared. Rosenfeld and Beath (157) reported normal litters from mothers receiving 1.5 to 2.5 p.p.m. of selenium in their diets.

The pathology of selenium poisoning seen in small animals—rat, rabbit, cat, and dog—is amazingly similar to that seen in farm animals—cattle, horse, and swine. Smith, Stohlman, and Lillie (169), in a detailed study of the pathology in selenized rat, found that the injury to the gastrointestinal tract, heart, spleen, kidney, and liver was similar to that seen in the large animal. They also observed a severe hypochromatic and microcytic anemia, bone-marrow hypoplasia with compensatory myeloid metaplasia of the liver and spleen. The histogenesis of liver cirrhosis, the most prominent lesion in selenium poisoning, was studied by Lillie and Smith (112). These authors observed that capillary congestion, focal and diffuse, developed into a hemorrhagic condition that was often periportal in location. These areas gradually became organizing hemorrhages with fibroblastic proliferation occluding clumps of surviving liver cells. Eventually dense fibrosis developed with the isolated parenchymal cells proliferating to form nodular cirrhosis.

Rhian and Moxon (151) reported that the hair of dogs fed selenium was coarse and loose, that walking was difficult and painful, that response to commands was slow, that the eyes were dull and lifeless, and that the dogs stumbled over objects blindly. The pathological findings were comparable to those seen in subacute poisoning of cattle.

Moxon and Rhian (131) have summarized the experiments conducted with small animals and reported through 1943. Some of the tolerances and characteristics of species other than the rat follow:

**Chicks.**—In the ration of young chicks 8 p.p.m. of selenium as sodium selenite retarded growth, but 4 p.p.m. had no effect. Selenium injected into fertile eggs in amounts as low as 0.0005 milligram per egg caused typical deformed embryos. Ra-



TABLE 23.—*Levels of selenium in the ration associated with different degrees of toxicity in various animals*

Animal	Amount of selenium and source of data for—		
	Acute toxicity <sup>1</sup>	Subacute toxicity	Chronic toxicity
Chicken.....	-----	-----	5 to 8 p.p.m. (131). <sup>2</sup>
Cow.....	4.5 to 5 mg. (120) <sup>3</sup>	-----	5 to 40 p.p.m. (123). <sup>3 4</sup>
Dog.....	20 p.p.m. (131) <sup>2</sup>	-----	7.2 to 10 p.p.m. (131). <sup>2</sup>
Frog.....	0.1 mg. (131)	-----	-----
Horse.....	1.5 mg. (120) <sup>3</sup>	-----	-----
Mule.....	1.5 mg. (120) <sup>3</sup>	-----	-----
Rat.....	4 mg. (118) <sup>5</sup>	15 to 25 p.p.m. (131) <sup>2</sup>	5 to 15 p.p.m. (131). <sup>2</sup>
Sheep.....	20 to 30 mg. (156) <sup>6</sup> per day	15 to 20 mg. per day (156) <sup>7</sup>	10 mg. per day (156).
Swine.....	6 to 8 mg. (120) <sup>3</sup>	-----	10 to 15 p.p.m. (131). <sup>2</sup>

<sup>1</sup> Generally lethal within 24 hours.

<sup>2</sup> In the ration.

<sup>3</sup> Per pound of body weight; sodium selenite administered orally.

<sup>4</sup> Over a period of several days to weeks.

<sup>5</sup> Death within 5 days.

<sup>6</sup> Dependent upon protein level, death in 13–30 days.

<sup>7</sup> Dependent upon protein level.

tions containing seleniferous grains (15 p.p.m. selenium in the ration) resulted in low hatchability of the eggs.

**Rabbit.**—By subcutaneous, intraperitoneal, or intravenous injection, the fatal dose of sodium selenite for the rabbit is from 0.9 to 1.5 milligrams of selenium per kilogram of body weight. The quantity of sodium selenate required is somewhat larger, 2.0 to 2.5 milligrams.

**Dog.**—The lethal dose for the dog is about 2 milligrams of selenium per kilogram of body weight by subcutaneous, intraperitoneal, or intravenous injection.

## EXPERIMENTAL WORK WITH LARGE ANIMALS

Miller and Williams (120) have shown that the single minimum lethal dose for horses and mules is about 1.5 milligrams of selenium per pound of body weight. The selenium as sodium selenite was administered orally. The minimum lethal dose for cattle was between 4.5 to 5 milligrams per pound of body weight, and for swine 6 to 8 milligrams. Other data on the quantities of selenium associated with degrees of toxicity in different animals are presented in table 23.

## PROTECTIVE MEASURES AGAINST SELENIUM

Supplements of calcium, phosphorus, cod liver oil, orange juice, and yeast had no effect on selenium toxicity in experiments reported by Moxon (123). Additions of cystine, fat, and sulfur to the diet were also without effect. In a diet containing 55 percent of protein plus 37.5 p.p.m. of

selenium, however, rats made slightly better gains than those on a 10-percent protein diet. On the basis of work by a number of workers, Moxon and Rhian (131) concluded that the protein content of the diet was of considerable importance as affecting toxicity of selenium to animals. They noted that proteins producing definitely favorable effects are casein, lactalbumin, ovalbumin, gelatine, and proteins derived from wheat, dried brewers' yeast, dessiccated liver, and zein. Rosenfeld and Beath (156, 157, 158) studied further the effect of protein, using sheep with controlled diets but simulating field conditions. Even at the high level of protein (20 percent digestible protein), only partial protection against selenium toxicity was obtained. Thus, 10 and 15 milligrams per day of selenium resulted in greatly decreased food intake. Toxic symptoms appeared in the high and medium protein-diet groups after the administration of 20 milligrams of selenium for 25 days, and in the low protein group (1.5 percent digestible protein) after 15 milligrams of selenium for 6 days. In the high and medium protein-diet group, death occurred after feeding 20 milligrams of selenium daily for 40 days, with a decrease of food intake of 90 percent or over. In these animals (157) there was a gradual decrease in the vitamin A and total protein content of the blood and a more rapid decrease in ascorbic acid. An increase of non-protein nitrogen in the blood was observed in all animals that died from selenium poisoning. Rosenfeld and Beath postulated that the increased resistance against selenium poisoning in animals fed high protein diets may be caused by the more complete saturation of the liver cells with protein producing a protection against injury of the cell by the toxic action of selenium. Moxon and Rhian (131) had noted that linseed meal and crude casein

were the more effective protein materials in reducing selenium toxicity. Halverson, Hendrick, and Olson (75) have reported, however, that the active principle of linseed oil meal may not be the protein. A hot 50-percent ethanol extract of linseed meal contained much of the protective principle. It was found to be volatile and water soluble, and an excess of lead did not precipitate it from solution.

Arsenic administered in the drinking water completely inhibited the toxicity of selenium to rats, according to Moxon (124). Subsequent work with the chick showed this treatment less successful than with rats and dogs (131). Moxon and Wilson (132) reported that 2.5 p.p.m. of arsenic counteracted in part the effect of selenium on the hatchability of eggs, 5 p.p.m. was somewhat better, but complete elimination of the effects of selenium was not obtained. Further work by Hendrick and Olson (76) indicates that sodium methyl arsenate and calcium methyl arsenate have no protective effect to rats fed a seleniferous diet. The arsenics were administered through the drinking water at the rate of 15 p.p.m. arsenic. In a later report (33) Olson and coworkers reported that 3-nitro-4-hydroxyphenylarsonic acid added to a basal diet of seleniferous corn fed to chicks resulted in greatly improved growth. The addition of B<sub>12</sub> (20 micrograms per pound) resulted in a nearly doubled growth in chicks, and selenium added to this diet had a much more pronounced toxic effect than it did on chicks fed the basal diet. Arsenicals added to the B<sub>12</sub> diet did not protect against selenium. Experiments with pigs (199) showed some protective effect of both 3-nitro-4-hydroxyphenylarsonic acid and arsanilic acid when added to a diet containing 10 p.p.m. of selenium. At higher levels of selenium (13 p.p.m.) the arsenicals did not entirely prevent toxicity symptoms unless linseed oilmeal was the source of protein. However, use of this protein supplement resulted in poorer growth and feed efficiency than did the use of soybean oilmeal.

## FAVORABLE EFFECTS OF SELENIUM IN THE DIET

An early reference, indicating a favorable effect of selenium on reproduction in rats, has been cited (133). Poley (145) claimed an indication of improved growth in chicks when 2 p.p.m. of selenium had been added to the diet. Recently, Patterson, Milstrey, and Stokstad (142), Schwarz, Bieri, Briggs, and Scott (161), and Schwarz and Foltz (162) have presented evidence that selenium will prevent exudative diathesis in chicks or liver damage in rats on a diet deficient in vitamin E and low in cystine. Selenium in the form of selenocystathionine (isolated by Horn and Jones (80) from *Astragalus pectinatus* in 1941) or as sodium selenite were equally effective. About 10 micrograms of selenium as the seleno-cystathionine, 13.3

micrograms as sodium selenite, or 4 micrograms of elemental selenium per 100 grams of diet all appeared to be effective. The preventive dose is about 1 percent of the chronic toxicity dose of 300–400 micrograms per 100 grams of ration. Under these conditions selenium appears to be about 500 times as active as vitamin E. There is no evidence that the need for selenium can be replaced by vitamin E, but diets very low in selenium and containing vitamin E are effective in preventing exudative diathesis. Patterson and coworkers (142) point out that Poley's favorable results with selenium in chick diets might have been due to the vitamin E present.

It is well known that some confusion exists regarding the relationship between metabolism of vitamin E and traces of selenium.

Muth, Oldfield, Remmert, and Schubert (134) have demonstrated that muscular dystrophy ("white muscle disease") in lambs can be prevented by supplementing the ewe's ration (legume hay and oats) with 0.1 p.p.m. selenium. Moreover, it was shown that treatment, orally or parenterally, of the ewe with alpha tocopherol (vitamin E) preparations at approximately physiological levels did not prevent a myopathy developing. Hogue (77) also presents evidence for the efficacy of selenium supplements in prevention of "stiff lamb disease." In this study vitamin E supplements at similar levels to those used by Muth were partially effective in protecting against the dystrophic condition.

## SELENIUM AND HUMAN NUTRITION

Selenium toxicity in humans has been carefully considered by the U.S. Public Health Service, whose members worked in severely selenized areas of Western States (167, 171). Conclusions are neither definitely positive nor certainly negative. Symptoms comparable to those of selenized domestic animals are essentially lacking. On the other hand, cases of arthritis appear to be associated with selenium in the diet. Degenerative processes in the liver may have been hastened. There is some suspicion that other features, such as discoloration of skin, bad teeth, dermatitis and gastrointestinal disorders, may be aggravated by the intake of small amounts of selenium. In the Irapuata area of Mexico strongly seleniferous vegetation is sold in local markets. Among the items collected at a market were radish roots—15 p.p.m. Se; spinach—7; and cabbage—70 (25). This area of Mexico was suggested as one especially suited for study of human ailments in relation to selenium. Such studies, however, have not been made. Tradition in the area indicates that human ill health has been related to outwash from silver mines. Since mercury was used in recovering silver, the presumption was that this element was

responsible for the trouble. As a matter of fact, seleniferous vegetation probably has caused some trouble there.

## CONCLUSIONS

Whereas the conditions for producing selenium toxicity in the laboratory animal and the chick have been fairly well established, the relationships in the grazing animal are less clear. The various degrees of toxicity in cattle encountered on the range are the results of the quantity of selenium ingested as well as the proportion and length of time that seleniferous vegetation is eaten. It would appear, however, that 5 p.p.m. or more selenium in vegetation should be considered as dangerous when ingested by any animal species over a period of several weeks.

The mechanism of the protective action of protein feeds against selenium is not clear, since con-

siderable variability in results with different species and different sources of protein have been experienced. Furthermore, more recent work indicates that the protein in one of the more protective materials, linseed oilmeal, may not be the active ingredient.

Likewise, the mechanism and effectiveness of the arsenicals needs further clarification. Experimentation with the less toxic organic compounds of arsenic has met with some success, although the results with different compounds are quite variable.

Of considerable interest are the recent experiments indicating the need for selenium by the rat and the chick when fed a vitamin E deficient diet and the effectiveness of selenium in preventing muscular dystrophy in lambs. Although this fact in itself does not establish selenium as an essential element for these species, it does suggest a sparing action of this element for vitamin E.

## Management of Seleniferous Lands

By M. S. ANDERSON

Investigations of selenium in soils as related to quality of vegetation and to animal sickness were well underway by the mid-1930's. At that time it had been shown that lands in certain Western States frequently produced forage and sometimes grain crops that were a hazard to the health of domestic animals. Such conditions reacted seriously against the economic welfare of local farmers and ranchers using these soils. Certain areas in South Dakota had been clearly delineated as having extensive seleniferous lands. It was established, also, that currently followed agricultural practices were not conducive to soil conservation nor did they give satisfactory economic return to the local farm operators over a period of years. It seemed desirable, therefore, to consider purchase of an extensive tract of these lands by Federal agencies for the purpose of establishing field practices in accordance with the best methods then known for the area. Furthermore, there seemed to be widespread advantages from possession of a large continuous area in which experiments might be conducted, if so desired, by Federal and State agencies.

## ACQUISITION OF LANDS

In 1935, at the request of local people, the recently organized Resettlement Administration of the Federal Government initiated proceedings for the purchase of farm and ranch lands then privately owned. The area lies south and a little west of Pierre, S. Dak. Average annual rainfall of the area is approximately 17 to 20 inches. Certain kinds of vegetation grown on the soils are

frequently seleniferous and injurious to farm animals. The soils are mostly of high clay content, difficult to work, and known locally as "gumbo." A discussion of Federal land projects in South Dakota is given by Glover (70).

In 1936 purchase of a large area of these lands in three counties of South Dakota by the Federal Government was accomplished. These lands are located as follows: In Lyman County 60,285 acres; in Stanley County 35,823 acres; and in Jones County 19,711 acres; total 115,819 acres. The area is known as the South Central South Dakota LU Project No. 2. Figure 12 shows the location of the lands in the State with respect to certain landmarks included for identification of the area. The average purchase price was \$5.80 per acre. During succeeding years a little more than the original purchase price has been expended for improvements in the area, primarily for cross fences and stock-water reservoirs.

The land purchased had been partly open-range country and partly fenced for farm use. About 75 homes had been established in the area, but only about 40 were occupied at the time of purchase by the Government. When the Federal Government took over the lands, it was during a period of unusually low rainfall in much of the Great Plains area. The United States, as a whole, was then in a period of deep economic depression. A number of the local farmers of these counties had moved away, and those remaining had no funds from current income to carry out soil conservation practices. Wind erosion was rampant. A photograph of a landscape within this area is shown in figure 13.

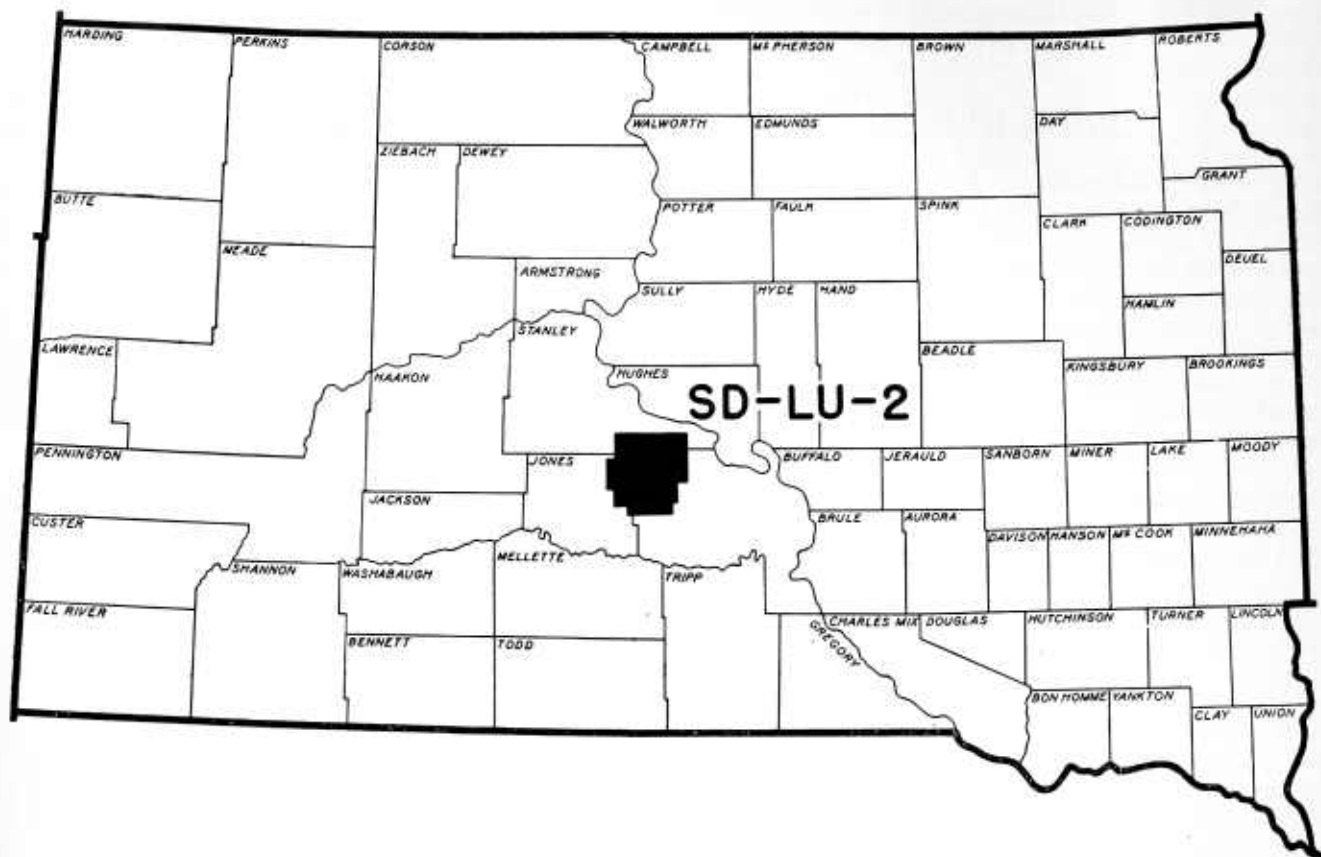


Figure 12.—Area SD-LU-2 shows the location of federally owned seleniferous lands in South Dakota. The total area of 115,819 acres is administered by the Forest Service.

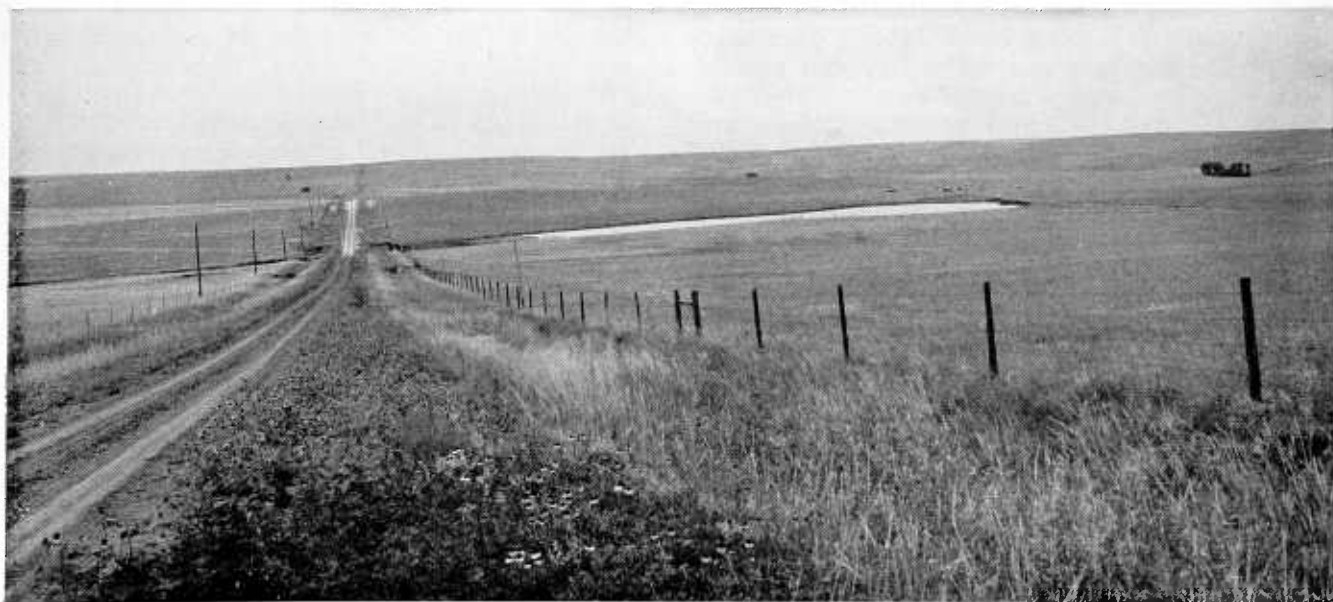


Figure 13.—Landscape, showing an extensive seleniferous area in South Dakota.

## LAND MANAGEMENT PRACTICES

Initial supervision of the newly acquired lands was assigned to different governmental agencies, particularly to the former Bureau of Agricultural Economics and the Soil Conservation Service of the U.S. Department of Agriculture. In 1954 responsibility for administration of the entire area was transferred to the Forest Service, which agency has extensive responsibility for the supervision of Federal lands for multiple-use management, including grazing.

Initial management practices consisted of removal of all farm buildings and some of the fences. Land that had once been plowed was properly treated for abatement of wind and water erosion. It was then put in proper condition and seeded with crested wheatgrass or other adapted forage vegetation. The cost of soil-improving practices since purchase has been moderately in excess of the original purchase price of the land.

Although the lands have not been used to any great extent for formal experimentation, much has been learned from continued operation of the practices initiated there. Some of these accomplishments are summarized by Dinkel and associates (44). These have led to a better understanding of desirable field management methods within the area. Seeding and grazing practices have increased the production of good-quality forage, the selenium contents of which appear not to interfere with normal animal health and weight gains as much as was the case before public ownership and management took place. Plant population counts have not been reported, but troublesome species of *Astragalus* plants presumably constitute a smaller portion of the total vegetation than was the case before the present management program was undertaken.

## GRAZING LEASE PRACTICES

It has been the custom of Federal agencies in charge of land utilization projects to lease the areas for immediate supervision by a local grazing district that handles the grazing contracts. During the fiscal year 1957 rentals for grazing privileges were reported to be approximately 18 cents per acre on the South Central Dakota Land Utilization Project. Counties where land is located receive 25 percent of the rental fees in lieu of taxes.

## THE EXAMPLE AND THE FUTURE

The management of Government-owned seleniferous lands in South Dakota has served as a demonstration ground rather than an intensively experimental one. Farmers and ranchers located on seleniferous lands elsewhere can now come to this great area in South Dakota to observe what may be accomplished by good range practice applied to seleniferous lands. Animal disease troubles incident to selenium are not entirely eliminated, but conditions are greatly improved.

One cannot look to this area for substantial agricultural profits; such was never the case. Low rainfall, stiff clay soils, cold winter temperatures, and the presence of excessive contents of selenium in a considerable portion of the soils all add to difficulties of profitable livestock production.

The foregoing discussion pertains only to three counties in South Dakota. Other areas within the State have seleniferous soils, as do certain areas in other Western States. The land acquired by the Federal Government probably represents one of the largest continuous areas where selenium troubles are pronounced. But even here not all of the soils are sufficiently seleniferous to make trouble for farmers.

## Summary

Selenium in certain soils of the Great Plains and other areas of the West is recognized as the cause of so-called alkali disease of domestic animals in the region. Range animals are most likely to be affected, particularly when the supply of good forage is limited and there is little opportunity for the animal to make any selection of forage types.

Soils associated with selenium trouble are derived, for the most part, from rocks of the Cretaceous age. Geology and mineralogy are related in important ways to the occurrence of selenium in rocks, soils, and plants. Highly seleniferous rocks are often of tuff, shale, or limestone groups. A vertical section of rock often shows wide variation of selenium content with depth. Considerable quantities of selenium are

transported in the drainage waters of certain western streams.

Rainfall in excess of about 25 inches appears to be sufficient to leach out the readily soluble and available selenium. Likewise, irrigation after several years will leach substantial quantities of the element from the soils, thus reducing the hazard.

Although the presence of selenium in plants has long been suspected, it was not until 1933 that quantitative estimations were made in the U.S. Department of Agriculture. Many thousands of analyses have since been reported in the literature for the purpose of determining the presence of quantities toxic to either man or animals. In the course of such survey studies it was soon learned

that typical selenium accumulator plants such as some members of the *Astragalus* genus (a legume), woody aster (a composite), and *Stanleya pinnata* (a mustard) were commonly found on seleniferous soils. Other plants, such as the cereals, also take up appreciable quantities of selenium if the element is in an available form in the soil.

The form of selenium in plants has never been clarified, although some of the early work indicated that it was present as a seleno-amino acid similar to cystine and leucine. The quantities of selenium reported range from 0.1 p.p.m. to several thousand p.p.m.

Extensive studies of the effects of toxic quantities of selenium on animals have been made. Horses, cattle, swine, and poultry are all susceptible to selenium poisoning. Both chronic and acute conditions have been recognized. The pathology of these conditions are described. Symptoms of toxicity may appear in a few hours or after several weeks, depending upon the quantity of selenium ingested. Death generally occurs in the acute cases, but, lameness, loss of hair, refusal to walk, and consequent troubles are seen in the milder cases. Congenital malformations in lambs and chicks are commonly found. Lethal doses for several animals have been established.

No practical protective measures are available except to limit grazing in certain areas. On federally owned lands in South Dakota, enough dry forage is left in the late fall to provide early pasturage for animals the next spring. Avoidance by grazing animals of early-growing toxic plants is thus made reasonably effective. The use of arsenic as a drench will counteract the effects of selenium, but this method requires careful control.

Some current investigations of certain diseases, such as muscular dystrophy ("white muscle disease") in lambs and calves, exudative diathesis in chicks, and liver damage in rats, indicate that small quantities of selenium will prevent such troubles. Extensive investigations must be made, however, before the essentiality of selenium is proved.

Methods for the chemical determination of selenium in different kinds of materials are given. These methods have been successfully used for more than 25 years as a means of determining selenium in soils, vegetation, and other materials. Methods for evaluating traces of the element are being currently investigated at several laboratories.

Selenium compounds as insecticides are discussed and the dangers arising from their use noted.

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# Appendix

By K. C. BEESON

The extensive investigations by the U.S. Department of Agriculture and several State Experiment Stations of the occurrence of seleniferous areas are reported in many bulletins and papers. To augment the search for work done in a par-

ticular area, references have been compiled in table 24 by States and counties. No interpretation of the data in terms of toxic or normal areas has been made. This information can best be obtained by a study of the original report.

TABLE 24.—*Locations by States and counties where the concentration of selenium in vegetation has been investigated*

State and county	Reference and page	State and county	Reference and page
Arizona:		Colorado—Cont.	
Apache.....	(14, p. 298)	Logan.....	(23, p. 31)
Cochise.....	(14, p. 298; 23, p. 35)	Mesa.....	(14, p. 301; 15, p. 892; 23, p. 32; 24, p. 19)
Coconino.....	(14, p. 298; 15, p. 892)	Moffat.....	(14, p. 302; 15, p. 892; 23, p. 32)
Gila.....	(14, p. 298)	Montezuma.....	(14, p. 301; 27, p. 66)
Greenlee.....	(14, p. 298)	Montrose.....	(23, p. 32; 24, p. 21)
Mohave.....	(14, p. 298; 15, p. 892)	Morgan.....	(23, p. 31; 27, p. 6)
Navajo.....	(14, p. 298; 27, p. 10)	Otero.....	(23, p. 31; 27, pp. 6, 17, 28; 205, p. 200; 209, pp. 8, 32, 42)
Pima.....	(14, p. 298; 15, p. 892; 23, p. 35)	Ouray.....	(14, p. 301; 23, p. 32)
Pinal.....	(15, p. 892)	Park.....	(14, p. 302)
Yavapai.....	(14, p. 298; 15, p. 892)	Prowers.....	(27, pp. 15, 26; 209, pp. 8, 32, 42)
California:		Pueblo.....	(27, p. 20)
Alameda.....	(101, p. 5)	Rio Blanco.....	(14, p. 301; 15, p. 892; 23, p. 32)
Colusa.....	(101, p. 5)	Routt.....	(14, p. 302; 23, p. 32)
Fresno.....	(101, p. 4)	San Miguel.....	(23, p. 32)
Glen.....	(101, p. 6)	Washington.....	(27, p. 6)
Kern.....	(101, p. 4)	Idaho:	
Los Angeles.....	(101, p. 3)	Ada.....	(14, p. 304)
Merced.....	(101, p. 4)	Bannock.....	(14, p. 304)
Napa.....	(101, p. 5)	Caribou.....	(106, p. 24)
Orange.....	(101, p. 3)	Clark.....	(14, p. 304)
San Bernardino.....	(101, p. 299)	Elmore.....	(102, pp. 23, 24; 209, p. 62)
San Joaquin.....	(101, p. 5)	Gem.....	(102, p. 23)
San Luis Obispo.....	(101, p. 4)	Gooding.....	(14, p. 304; 102, p. 24; 209, p. 62)
Santa Barbara.....	(101, p. 4)	Owyhee.....	(14, p. 304; 102, p. 23; 209, p. 62)
Solano.....	(101, p. 5)	Power.....	(14, p. 304)
Stanislaus.....	(101, p. 4)	Twin Falls.....	(102, p. 23)
Tehama.....	(101, p. 6)	Kansas:	
Yolo.....	(101, p. 5)	Barber.....	(23, p. 34)
Colorado:		Clark.....	(23, p. 34)
Adams.....	(23, p. 31)	Comanche.....	(23, p. 34)
Archuleta.....	(14, p. 301; 15, p. 892)	Gove.....	(23, p. 34; 24, p. 40; 205, p. 200; 209, p. 8)
Bent.....	(27, pp. 6, 16, 27, 42; 209, pp. 8, 32, 42)	Graham.....	(24, p. 45; 209, p. 8)
Cheyenne.....	(27, p. 6; 209, pp. 32, 42)	Hamilton.....	(23, p. 34)
Crowley.....	(27, pp. 6, 18; 209, pp. 32, 42)	Lane.....	(208, p. 8)
Delta.....	(24, p. 21)	Logan.....	(23, p. 34; 24, p. 29; 209, pp. 8, 32, 42, 64)
El Paso.....	(14, p. 301; 27, pp. 6, 21, 45; 205, p. 200)	Ness.....	(209, p. 9)
Fremont.....	(14, p. 301; 27, pp. 6, 22)	Norton.....	(24, p. 48)
Garfield.....	(15, p. 893; 23, p. 31)	Phillips.....	(24, p. 48; 209, p. 9)
Grand.....	(14, p. 301; 15, p. 892; 23, p. 31)	Rooks.....	(24, p. 46; 209, p. 9)
Gunnison.....	(23, p. 32)	Scott.....	(24, p. 43)
Huerfano.....	(14, p. 302; 27, pp. 6, 19, 44)	Trego.....	(24, p. 43; 209, p. 9)
Kiowa.....	(27, pp. 6, 15, 63; 119, p. 65; 205, p. 200; 209, pp. 32, 42, 63)	Wallace.....	(23, p. 34; 24, p. 27; 209, pp. 9, 32)
La Plata.....	(14, p. 301)	Montana:	
Larimer.....	(14, p. 301; 15, p. 892; 23, p. 31)	Big Horn.....	(14, p. 306; 15, p. 893; 208, p. 9; 209, pp. 9, 33, 42)
Las Animas.....	(14, p. 302; 23, p. 31; 27, p. 19)		
Lincoln.....	(14, p. 301; 23, p. 31; 27, pp. 6, 18)		

TABLE 24.—*Locations by States and counties where the concentration of selenium in vegetation has been investigated—Continued*

State and county	Reference and page	State and county	Reference and page
Montana—Con.		New Mexico—Con.	
Blaine	(14, p. 306; 209, pp. 10, 33)	Dona Ana	(14, p. 309)
Carter	(14, p. 306; 15, p. 893; 23, p. 28; 24, p. 15; 209, pp. 10, 33, 42)	Harding	(14, p. 309; 27, p. 34)
Cascade	(14, p. 306; 15, p. 894; 208, p. 28; 209, pp. 10, 33, 42)	Hidalgo	(14, p. 309)
Chouteau	(14, p. 306; 208, p. 24; 209, pp. 11, 33)	Lincoln	(14, p. 309)
Daniels	(15, p. 893; 209, pp. 12, 43)	Luna	(14, p. 309)
Dawson	(14, p. 307)	McKinley	(14, p. 309; 15, p. 894)
Deer Lodge	(14, p. 306)	Mora	(27, pp. 8, 33)
Fergus	(15, p. 894; 208, p. 26; 209, pp. 12, 33)	Otero	(14, p. 309; 15, p. 894)
Gallatin	(14, p. 306)	Quay	(14, p. 309)
Garfield	(15, p. 893; 209, p. 63)	Rio Arriba	(14, p. 309; 15, p. 894; 27, p. 8)
Glacier	(14, p. 306; 209, pp. 13, 33, 43)	Sandoval	(14, p. 309; 15, p. 894)
Hill	(14, p. 306; 15, p. 893; 208, p. 29; 209, pp. 13, 33, 43)	San Juan	(14, p. 309; 15, p. 894; 27, p. 8)
Jefferson	(14, p. 306)	San Miguel	(27, pp. 8, 34)
Judith Basin	(15, p. 894; 208, p. 29; 209, p. 13)	Santa Fe	(14, p. 309; 15, p. 894; 27, p. 8)
Lewis and Clark	(208, p. 28)	Sierra	(14, p. 309)
Liberty	(15, p. 894; 209, pp. 13, 43)	Socorro	(14, p. 309; 15, p. 894)
McCone	(14, p. 306; 15, p. 893)	Taos	(15, p. 894)
Musselshell	(15, p. 893)	Torrance	(15, p. 894)
Petroleum	(209, pp. 14, 33, 63)	Union	(15, p. 894)
Phillips	(24, p. 58; 209, pp. 14, 33, 43)	North Dakota:	
Pondera	(14, p. 306; 15, p. 894; 208, p. 21; 209, pp. 14, 34, 43, 64)	Bottineau	(102, p. 4)
Roosevelt	(14, p. 306; 15, p. 893; 209, p. 14)	Burke	(102, p. 5; 209, p. 55)
Rosebud	(15, p. 893; 208, p. 14)	Burleigh	(209, p. 18)
Sheridan	(15, p. 893; 209, pp. 15, 34)	Cavalier	(102, p. 6)
Teton	(14, p. 306; 15, p. 894; 208, p. 15; 209, pp. 15, 34, 43, 57)	Dickey	(102, p. 6)
Toole	(14, p. 306; 15, p. 894; 209, p. 15)	Divide	(102, p. 6)
Treasure	(15, p. 893)	Golden Valley	(14, p. 310)
Valley	(14, p. 306; 24, p. 58; 209, pp. 15; 44)	McHenry	(102, p. 7)
Wheatland	(15, p. 893)	McKenzie	(102, p. 7)
Yellowstone	(14, p. 307; 15, p. 893; 208, p. 12; 209, pp. 16, 34, 44)	McLean	(102, p. 7)
Nebraska:		Mountrail	(102, p. 8; 207, pp. 18, 35, 44, 55)
Boyd	(15, p. 894; 23, p. 33; 129, pp. 49, 69; 209, pp. 17, 34)	Pierce	(102, p. 9)
Cedar	(23, p. 33; 209, pp. 35, 63)	Renville	(102, p. 9)
Dawes	(24, p. 6; 209, pp. 17, 35, 44, 63)	Sheridan	(102, p. 10)
Dundy	(15, p. 894; 23, p. 33)	Stutsman	(15, p. 894)
Franklin	(15, p. 894; 23, p. 33)	Ward	(102, p. 10; 209, pp. 19, 36, 44, 56)
Furnas	(23, p. 33; 209, pp. 17, 35)	Williams	(102, p. 11; 209, pp. 19, 44, 56)
Harlan	(15, p. 894; 23, p. 33; 209, p. 17)	Oklahoma:	
Hitchcock	(15, p. 894; 23, p. 33; 209, p. 17)	Bryan	(101, p. 14)
Knox	(23, p. 33; 209, pp. 18, 35)	Caddo	(23, p. 34; 101, p. 13)
Nance	(209, p. 63)	Cleveland	(23, p. 34)
Red Willow	(15, p. 894; 209, p. 18)	Custer	(101, p. 13)
Sheridan	(24, p. 6; 209, pp. 18, 35)	Grady	(23, p. 34; 101, p. 14)
Sioux	(24, p. 9; 209, p. 18)	Kiowa	(101, p. 13)
Webster	(15, p. 894; 23, p. 33)	Washita	(101, p. 13)
Nevada:		Oregon:	
Clark	(14, p. 307; 101, p. 10; 102, pp. 22, 23)	Harney	(14, p. 310)
Douglas	(14, p. 307)	Malheur	(102, p. 24)
Elko	(14, p. 307; 102, p. 22)	Puerto Rico	(27, p. 65; 208, p. 49)
Humboldt	(14, p. 307)	South Dakota:	
Lincoln	(14, p. 307)	Beadle	(163, p. 461; 164, p. 28)
Lyon	(14, p. 307)	Brookings	(163, p. 461; 164, p. 28)
Mineral	(14, p. 307)	Brule	(15, p. 896; 23, p. 30; 209, pp. 20, 36)
Nye	(14, p. 307)	Butte	(15, p. 894; 23, pp. 29, 36; 24, p. 16; 129, pp. 31, 38, 79; 204, p. 203; 209, pp. 20, 36, 44)
Pershing	(14, p. 307)	Charles Mix	(23, p. 30; 129, p. 50)
White Pine	(14, p. 307; 102, p. 22)	Codington	(163, p. 461; 164, p. 28)
New Mexico:		Corson	(129, p. 54)
Catron	(14, p. 309; 15, p. 894)	Custer	(24, p. 16; 129, p. 38; 209, p. 36)
Colfax	(14, p. 309; 15, p. 894; 27, pp. 8, 32)	Day	(163, p. 461; 164, p. 28)
De Baca	(14, p. 309)	Dewey	(23, p. 29)
		Fall River	(14, p. 311; 24, p. 12; 129, pp. 30, 37, 55, 79; 209, pp. 21, 36, 45)
		Gregory	(14, p. 311; 15, p. 894; 23, pp. 13, 42; 24, p. 66; 129, pp. 49, 70; 209, pp. 21, 36, 62)
		Haakon	(14, p. 311; 129, p. 53; 209, p. 21)
		Hughes	(14, p. 311; 23, p. 30; 209, pp. 22, 37)
		Hyde	(23, p. 30)



TABLE 24.—*Locations by States and counties where the concentration of selenium in vegetation has been investigated—Continued*

State and county	Reference and page	State and county	Reference and page
South Dakota—Con.		Utah—Continued	
Jackson-----	(14, p. 311; 129, pp. 53, 81; 209, p. 22)	Iron-----	(14, p. 313)
Jones-----	(14, p. 311; 23, p. 39; 209, pp. 22, 37)	Juab-----	(14, p. 313; 78, p. 299; 102, p. 21)
Kingsbury-----	(163, p. 461; 164, p. 28)	Millard-----	(14, p. 313; 78, p. 299; 102, pp. 21, 22)
Lawrence-----	(15, p. 896)	Piute-----	(102, p. 22)
Lyman-----	(14, p. 311; 23, pp. 17, 39; 24, p. 62; 101, p. 17; 129, pp. 35, 42, 51, 71, 77; 208, p. 55; 209, pp. 22, 37, 45, 62)	Rich-----	(14, p. 313)
Meade-----	(23, p. 29; 24, p. 16; 129, pp. 36, 69, 79; 209, pp. 23, 38)	Salt Lake-----	(102, p. 21)
Pennington-----	(14, p. 312; 23, p. 29; 24, p. 16; 129, pp. 36, 81; 209, pp. 23, 38)	San Juan-----	(14, p. 313)
Shannon-----	(14, p. 311; 24, p. 11; 129, p. 34)	Sevier-----	(102, pp. 21, 22)
Stanley-----	(14, p. 311; 129, pp. 52, 69, 79; 209, pp. 23, 38, 45, 63)	Summit-----	(102, p. 31)
Sully-----	(23, p. 30)	Tooele-----	(14, p. 313; 102, p. 21)
Tripp-----	(209, pp. 23, 38)	Uintah-----	(14, p. 313; 15, p. 896; 102, p. 21)
Walworth-----	(23, p. 29)	Utah-----	(14, p. 313; 102, p. 21)
Yankton-----	(14, p. 311)	Washington-----	(14, p. 313)
Ziebach-----	(23, p. 29; 129, p. 38; 130, p. 303)	Wayne-----	(15, p. 896)
Texas:		Wyoming:	
Brewster-----	(14, p. 312)	Albany-----	(15, p. 897; 23, p. 22)
Dallas-----	(15, p. 896)	Big Horn-----	(206, pp. 23, 38, 45)
Hill-----	(15, p. 896)	Campbell-----	(23, p. 27; 209, pp. 24, 38, 45)
Utah:		Carbon-----	(15, p. 898; 23, p. 25)
Beaver-----	(78, p. 299)	Converse-----	(209, pp. 24, 38)
Box Elder-----	(14, p. 313)	Crook-----	(23, p. 27; 24, p. 15; 209, pp. 24, 39, 45, 64)
Cache-----	(78, p. 299)	Fremont-----	(15, p. 897; 23, p. 26)
Carbon-----	(14, p. 313; 27, p. 10; 102, pp. 21, 22)	Hot Springs-----	(23, p. 27)
Duchesne-----	(14, p. 313; 15, p. 897)	Johnson-----	(209, pp. 24, 39)
Emery-----	(14, p. 313; 15, p. 896; 27, p. 10; 102, p. 22)	Natrona-----	(23, p. 26; 209, pp. 24, 39, 45)
Garfield-----	(7, p. 703; 27, p. 10)	Niobrara-----	(15, p. 898; 24, p. 14; 129, pp. 32, 39; 209, pp. 24, 39, 45)
Grand-----	(7, p. 703; 14, p. 313; 15, p. 896; 23, p. 35; p. 27, 10)	Platte-----	(15, p. 898)
		Sheridan-----	(23, p. 27; 209, pp. 25, 39)
		Sweetwater-----	(15, p. 898)
		Teton-----	(15, p. 898)
		Uinta-----	(15, p. 898; 23, p. 27)
		Washakie-----	(23, p. 27; 209, pp. 25, 39, 45)
		Weston-----	(24, p. 14; 209, pp. 25, 39, 45)



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